Second International Symposium on Theory of Atomic and Molecular Clusters
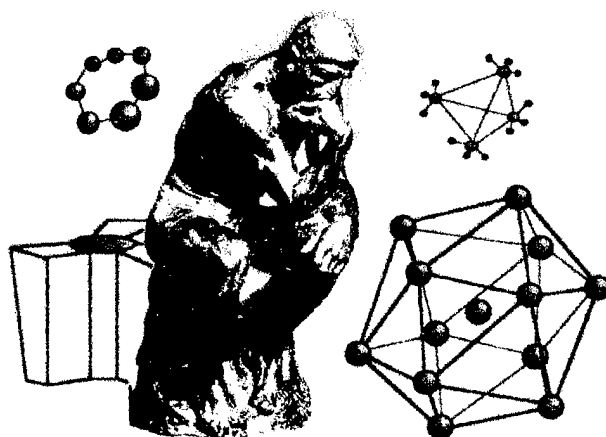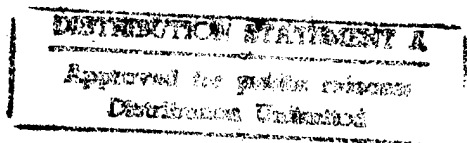

TAMC - 2

September 15-20, 1996
The Abbey on Lake Geneva Resort, Fontana, Wisconsin, USA

Book of Abstracts

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The Second International Symposium on the Theory of Atomic and Molecular
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The meeting attracted 86 participants, from North America, Europe,
Turkey, Israel, India and Japan. The full program included 32 oral
presentations, 43 posters and two roundtable discussions.

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Symposium Program

<center>Sunday, September 15</center>

5:00 p.m.   Registration / Welcome Reception

8:30   Dinner

<center>Monday, September 16</center>

8:20 a.m.   Opening Remarks

8:30   **D. Wales,** Chairman, University of Cambridge, UK

8:35   **Z. Bačić,** New York University, USA
Spectral Shifts and Photodissociation of HF in Ar_nHF (n=1-14,54) Clusters
9:05   Discussion

9:15   **L. Wöste,** Freie Universität, Berlin, Germany
Laser Spectroscopy of Metal Clusters
9:45   Discussion

9:55   Coffee Break

10:30   **R. B. Gerber,** Hebrew University of Jerusalem, Israel
Wavefunctions, Dynamics and Spectroscopy of Large Clusters
11:00   Discussion

11:10   **U. Landman,** Georgia Institute of Technology, USA
Clusters in Nanowires and Nanostructures
11:30   Discussion

11:35   **G. Seifert,** Technische Universität, Dresden, Germany
Ionization Energies, Stability and Fragmentation Dynamics of Fullerene Ions
11:55   Discussion

12:00   Lunch

4:30 p.m.   Coffee

4:50   **C. Guet,** Chairman, CEA - Grenoble, France

4:55   **W. L. Hase,** Wayne State University, USA
Collisional Excitation and Unimolecular Dissociation of Aluminum Clusters
5:25   Discussion

5:35   **M. J. López,** Universidad de Valladolid, Spain

<center>1</center>

	Fragmentation of Small Transition Metal Clusters: Dynamical Simulations and Statistical Models
5:55	Discussion
6:30	Dinner
7:45 - 9:30	Poster Session

Tuesday, September 17

8:30 a.m.	**E. R. Hilf,** Chairman, University of Oldenburg, Germany
8:35	**J. D. Doll,** Brown University, USA Theoretical Studies of the Structure and Dynamics of Metal/Hydrogen Systems: Diffusion and Path Integral Monte Carlo Investigations of Ni and Pd Clusters.
9:05	Discussion
9:15	**M. Jarrold,** Northwestern University, USA High Resolution Ion Mobility Studies of Atomic Clusters
9:45	Discussion
9:55	Coffee Break
10:30	**D. H. E. Gross,** Hahn-Meitner-Institut, Berlin, Germany The Role of Entropy in Cluster Fragmentation. Microcanonical Thermodynamics.
11:00	Discussion
11:10	**S. Srinivas,** Argonne National Laboratory, USA Ab Initio Monte Carlo: Application to Li_8
11:30	Discussion
11:35	**H.-P. Cheng,** University of Florida, Gainesville, USA The Motion of Protons in Water-Ammonia Clusters
11:55	Discussion
12:00	Lunch
2:00 p.m.	**K. H. Bennemann,** Chairman, Freie Universität, Berlin, Germany
2:05	**C. Yannouleas,** Georgia Institute of Technology, USA Triaxial Deformations and Temperature Effects in Fermionic Clusters
2:35	Discussion
2:45	**K. A. Jackson,** Central Michigan University, USA Density Functional-Based Raman and IR Spectra of Si Clusters
3:05	Discussion

3:10	**K. Raghavachari,** Bell Laboratories, USA
	Isomers of C_{20}: Is There a Reliable Theory?
3:30	Discussion

3:35 - 4:30   Coffee Break - Poster Session (cont.)

6:30   Dinner

8:00 - 9:30   <u>Roundtable Discussion:</u> Cluster Modeling, Calculations, Simulations: the State of the Art in Electronic Structure Calculations into the Next Millenium

Moderator:	**D. R. Salahub,**	Université de Montréal, Canada
Panelists:	**E. Carter,**	UCLA, USA,
	K. Raghavachari,	Bell Laboratories, USA,
	A. Rosén,	Chalmers University of Technology, Sweden,
	N. Russo,	Universitá della Calabria, Italy

Wednesday, September 18

8:30 a.m.	**U. Landman,** Chairman, Georgia Institute of Technology, USA

8:35	**C. Guet,** CEA - Grenoble, France
	Electron Dynamics in Metal Clusters: Vlasov Equation Approach
9:05	Discussion

9:15	**K. M. Ho,** Iowa State University, Ames, USA
	Structural Optimization of Atomic Clusters Using a Genetic Algorithm
9:45	Discussion

9:55	**I. Garzón,** UNAM, Ensenada, Mexico
	Structural and Vibrational Analysis of Amorphous Au_{55} Clusters
10:15	Discussion

10:20   Coffee Break

10:50	**G. M. Pastor,** Université de Paul Sabatier, France
	Magnetic Anisotropy of Transition Metal Clusters, Chains and Films
11:20	Discussion

11:30	**S. Khanna,** Virginia Commonwealth University, USA
	Recent Developments in the Theory of Magnetism in Clusters
11:50	Discussion

11:55	**T. Frauenheim,** Technische Universität, Dresden, Germany
	From Icosahedral Clusters to Polymeric Fullerenes

12:15	Discussion
12:20	Lunch
2:00 - 4:00 p.m.	Boat Trip
6:30	Dinner

8:00 - 9:30	<u>Roundtable Discussion:</u> Landscapes of Potential Energy Surfaces: Analyses and Consequences for Dynamics

	Moderator:	**R. S. Berry,**	University of Chicago, USA
	Panelists:	**I. Ohmine,**	Nagoya University, Japan,
		J. N. Onuchic,	University of California, San Diego, USA,
		D. Wales,	University of Cambridge, UK

Thursday, September 19

8:30 a.m.	**A. Rosén,** Chairman, Chalmers University of Technology, Sweden
8:35	**J. A. Alonso,** Universidad de Valladolid, Spain Clusters of Interest for Liquid Ionic Alloys
9:05	Discussion
9:15	**H. Häkkinen,** University of Jyväskylä, Finland Structure, Stability and Dynamics of Supported Metal Clusters
9:45	Discussion
9:55	Coffee Break
10:30	**P. Hackett,** Steacie Institute for Molecular Sciences, Canada Small Metal Clusters as Models for Reaction Sites on Surfaces
11:00	Discussion
11:10	**M. Moseler,** Freiburg Materials Research Center, Germany Cluster-Surface Collision: The Influence of Surface Orientation, and Electron-Phonon Coupling
11:30	Discussion
11:35	**R. J. Tarento,** Université Paris-Sud, France Electronic and Magnetic Properties in Mesoscopic Tubules and Permanent Current
11:55	Discussion
12:00	Lunch

2:00 p.m.	**M. Manninen,** Chairman, University of Jyväskylä, Finland
2:05	**V. Bonačić-Koutecký,** Humboldt Universität, Berlin, Germany
	Methods for Optical Control of Time-Dependent Processes in Clusters and Their
	Reactions
2:35	Discussion
2:45	**R. Kawai,** University of Alabama, Birmingham, USA
	Packing Transitions in the Growth of Alkali Metal Clusters
3:05	Discussion
3:10	Coffee Break
3:40	**M. E. Garcia,** Freie Universität, Berlin, Germany
	Ultrafast Dynamics of Small Clusters upon Ionization and Photodetachment
4:10	Discussion
4:20	**I. G. Kaplan,** UNAM, Mexico City, Mexico
	Ab Initio Model Potential for Molecular Dynamics Simulation of Metal Clusters;
	Application to Silver Hexamers
4:40	Discussion
7:30	Banquet

Friday, September 20

8:30 a.m.	**S. Khanna,** Chairman, Virginia Commonwealth University, USA
8:35	**P. Jena,** Virginia Commonwealth University, USA
	From Clusters to Cluster-Assembled Materials (tentative title)
9:05	Discussion
9:15	**J. R. Chelikowsky,** University of Minnesota, Minneapolis, USA
	Photoemission Spectra and Structures of Si and Ge Clusters at Finite Temperature
9:35	Discussion
9:40	Coffee Break
10:10	**J. Jortner,** Tel Aviv University, Israel
	Cluster Theory: What is New?
10:50	Discussion
11:00	Lunch
12:00	Departure

Invited Talks

SPECTRAL SHIFTS AND PHOTODISSOCIATION OF HF
IN Ar_nHF (n = 1 − 14, 54) CLUSTERS

Zlatko Bačić

Department of Chemistry, New York University, New York, NY 10003

Ar_nHF clusters provide an exemplary model system for studying how a solvent cluster (Ar_n) of increasing size modifies the spectroscopy and the photofragmentation dynamics of the solute molecule (HF). The global and low-lying local minima of Ar_nHF, $n = 1 - 14$, were determined using simulated annealing, for highly accurate pairwise additive potential energy surface (PES). The calculations, which combined the equilibrium Ar_nHF structures with quantum 5D treatment of HF vibrations in the Ar_n cluster (taken to be rigid), predicted that the HF vibrational frequency shift for Ar_nHF ($n = 1 - 14$) clusters had a distinctly nonmonotonic size dependence, and was strongly isomer specific as well. HF redshifts obtained for the additive PESs agree very well with the experimental data available for the $n = 1 - 4$ clusters. The quantum 5D results were confirmed by our full-dimensional diffusion quantum Monte Carlo calculations of the intermolecular vibrational ground states, structures, and HF redshifts of Ar_nHF clusters with $n = 1 - 4$. Subsequent inclusion of three-body interactions has brought the $n = 2 - 4$ HF redshifts into even beter agreement with experiment. A comprehensive study of the photodissociation of HF in Ar_nHF ($n = 1 - 14, 54$) clusters, for an ultrashort $\delta(t)$-pulse excitation, was performed. Classical trajectories were used to simulate the photodissociation dynamics. The probability distributions of the initial coordinates and momenta of the H and F atom were defined by accurate quantum 5D eigenstates of the large amplitude intermolecular vibrations of HF in the cluster. All aspects of the dissociation process studied, including the H-atom kinetic energy and angular distributions, the survival probability, and cluster fragmentation patterns, were found to exhibit a strong dependence on the size and geometry of the Ar_n solvent cluster.

Laser Spectroscopy of Metal Clusters

L. Wöste

Institut für Physik

Freie Universität Berlin

Berlin, Germany

The presentation will give a review on spectroscopy experiments on metal clusters beginning with simple resonant two-photon-ionization experiments. In detail this is discussed for the example of the sodium trimer. In larger aggregates electronic excitations are commonly followed by fragmentation processes. The observed band structures are significantly broadened and the intensities of the absorption lines scale roughly with the amount of valence electrons. Despite of that particles like Li_n (n < 8) must still be visualized as molecular systems. The broadened lineshapes result on one hand from a lifetime-related homogeneous contribution, on the other hand they are inhomogeneously broadened by the superposition of various rovibronic states, isomers and isotopomers. A specific observation of these phenomena is only possible by means of time resolved spectroscopy in the pico- and femtosecond regime. With respect to this the newly developed NeNePo method (negative-neutral-positive) is of particular interest, because it allows to observe the wave-packet dynamics in the electronic ground state of size selected neutral clusters. This provides not only the chance to probe the dynamics of a chosen particle in a real-time observation scheme, but it also allows to trace geometrical changes and reaction pathways of size selected particles.

Wavefunctions, Dynamics and Spectroscopy of Large Clusters

R. B. Gerber [a], [b] P. Junwirth[c], E. Fredj[a],[b]J. Jung[a],[b] and A. Roitberg[d]

(a) Department of Physical Chemistry, Hebrew University of Jerusalem, Jerusalem 91904, Israel
(b) Department of Chemistry, University of California, Irvine, Irvine, CA92697 USA
(c) J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic Dolejkora 3,18223 Prague 8, Czech Republic
(d) National Institute for Standards and Technology, Biochemistry Division, Gaithersberg, MD 20899, USA

Through the development of new methods, quantum-mechanical simulations of good accuracy of the dynamics of many atom clusters, at the detailed level of wavefunctions, are becoming possible. The lecture presents results on vibrational dynamics, spectroscopy, photophysical and collision processes of clusters, all studied by simulations of time-independent and time-dependent wavefunctions for many coupled degrees of freedom. Some of the main topics are:

1. *Vibrational wavefunctions and spectroscopy of the protein BPTI, and of related systems*: Using the Vibrational Self-Consistent Field (VSCF) method, anharmonic wavefunctions and spectroscopy of large clusters, including proteins[1]were obtained. For some large systems corrections of high accuracy beyond VSCF were also computed. One of the interesting results for the protein BPTI, is that the IR spectrum shows interesting low-frequency structure, corresponding to low-frequency collective and amharmonic modes.

2. *Time-dependent Quantum Molecular Dynamics of large clusters*: Such simulations were made possible by the Classical Separable Potential (CSP) approach(2), initiated as a simple approximation, but with improvements methods the basis of much more accurate calculations. This approach uses classical trajectory calculations to "guide" a multidimensional quantum simulation.

3.*Ultrafast photoinduced dynamics and Resonance Raman spectroscopy of $I_2(Ar)_n$, $I_2(Xe)_n$ clusters(3)*: These quantum simulations explain the enormous difference

between RR spectrum of isolated I_2, and that of "solvated" I_2, by detailed physical mechanisms. Also, quantitative agreement is obtained between large cluster calculations and metnix experiments.

4. *Equilibrium dynamics and photoexcitition behavior of Li(Ne)$_{17}$*: We show that time dependent quantum simulations can be pursued to <u>equilibration</u>, this yielding data on equilibrium dynamics. For Li(Ne)$_{17}$ the vibrational spectrum calculated at T=1K is found to be highly anharmonic, and highly non-classical. The excited state dynamics was also computed.

5. *Energy transfer in Ar+(H$_2$O)$_{11}$ collisions*: Quantum results for the state-specific inelastic collisions are obtained. Very large non-classical effects are found.

<u>References</u>

(1)   A. Roitberg, R.B. Gerber, R. Elber and M.A. Ratner, Science, 268, 1319 (1995)
(2)   P.Jungwirth and R. B. Gerber, J. Chem. Phys. <u>102</u>, 6046 (1995)
(3)   P. Jungwirth, E. Fredj and R.B. Gerber, J. Chem. Phys. (In Press)

Collisional Excitation and Unimolecular Dissociation of Aluminum Clusters

William L. Hase, Pascal de Sainte Claire and Gilles H. Peslherbe[a]

Monte Carlo, molecular dynamics, classical trajectory, and statistical theoretical (i.e., RRKM and phase space) methods are used to study the collision-induced dissociation (CID) and unimolecular dynamics of Al_n (n = 3, 6, 13) clusters, represented by a model analytic potential energy function. The efficiency of collisional energy transfer in CID is affected by the vibrational frequencies (i.e., stiffness) of the cluster, the repulsiveness of the intermolecular potential between the cluster and collision partner, and the relative translational energy. The classical intramolecular dynamics of the clusters is ergodic. Thus, the trajectory rate constants for dissociation of the clusters are in accord with RRKM theory, but much different than the predictions of the approximate harmonic model. The fluxional character of the aluminum clusters, with their multiple minima, makes their densities of states much larger than the harmonic oscillator value. The classical trajectory energy distributions for the Al_{n-1} + Al products agree with the predictions of phase space theory.

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[a] Current address: Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309.

Theoretical Studies of the Structure and Dynamics of Metal/Hydrogen Systems: Diffusion and Path Integral Monte Carlo Investigations of Ni and Pd Clusters.

B. Chen, M. A. Gomez, M. Sehl and J. D. Doll
Department of Chemistry, Brown University, Providence, RI 02912

David L. Freeman
Department of Chemistry, University of Rhode Island, Kingston, RI 02881

Using both classical and quantum mechanical Monte Carlo methods, a number of properties are investigated for a single hydrogen atom adsorbed on palladium and nickel clusters. In particular, the geometries, the preferred binding sites, site specific hydrogen normal mode frequencies and finite temperture effects in clusters from two to ten metal atoms are examined. Our studies indicate that hydrogen is localized in the present systems. The preferred hydrogen binding sites are found to be tetrahedral in clusters with five or fewer metal atoms and octahedral for clusters with six to ten atoms. The exceptions to this rule are $Ni_{10}H$ and Pd_9H for which the outside, three-fold hollow and the inside, tetrahedral sites are preferred, respectively. Hydrogen induced "reconstruction" of bare cluster geometries is seen in seven and ten-atom clusters.

High-Resolution Ion Mobility Studies Of Atomic Clusters

Ph. Dugourd, R. R. Hudgins and M. F. Jarrold
Department of Chemistry
Northwestern University
Evanston, IL

The development of a new high-resolution ion mobility apparatus will be described. The new apparatus is capable of over an order of magnitude higher resolving power than can be acheived in conventional ion mobility experiments. Studies of C, Si, and NaCl clusters will be reported. For the NaCl clusters, a wide variety of different shaped (n x k x l) cuboids are observed. Interconversion between geometries with very different cuboid dimensions occurs at, or slightly above, room temperature.

The role of entropy in cluster fragmentation.
— Microcanonical Thermodynamics —

D.H.E. Gross

Hahn-Meitner-Institut Berlin, Bereich Theoretische Physik,
14109 Berlin, Germany
and
Freie Universität Berlin

The general features of Microcanonical Thermodynamics as applied to the fragmentation of atomic clusters are discussed. Here we first develop the thermodynamics of microcanonical phase transitions of first and second order. We show how both kinds of phase transitions can unambiguously be identified in small isolated systems of ~ 100 atoms. In contrast to ordinary (canonical) thermodynamics Microcanonical Thermodynamics is able to describe inhomogeneous systems. Therefore it can give an insight into the coexistence region where the systems fragments into spatially separated regions of different phase. Here the form of the specific heat $c(E/N)$ connects transitions of first and second order in a natural way. The phase transition towards fragmentation is introduced. It is within Microcanonical Thermodynamics a clear transition of first order well seen in the caloric equation of state $T(E, V)$ at fixed volume V. We also show the microcanonical caloric equation of state $T(E, P = 1\mathrm{atm})$ of Na-clusters with rising number of atoms and discuss how the fragmentation transition and its basic parameters, the transition temperature T_{tr}, the specific latent heat q_{lat} and the interphase surface tension develop into the ones of the bulk liquid-gas transition. The similarities and differences of multifragmentation of finite clusters to the boiling of macrosystems are pointed out.

Triaxial deformations and temperature effects in fermionic clusters

Constantine Yannouleas and Uzi Landman

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430

We use the recently developed semiempirical shell-correction method [1] (SE-SCM) to calculate the binding energies of open-shell, simple-metal and ^{3}He clusters, which can be modeled as triaxially deformed droplets.

Systematics of ionization potentials, electron affinities, and second-energy differences are studied at zero temperature and compared to experimental measurements on sodium, potassium, and the noble-metal (Cu, Ag, Au) clusters. Systematics of the energetics of fission channels for doubly charged cations, as well as the energetics of monomer and dimer separation channels will also be reported. The topography of the Potential Energy Surfaces reveals the coexistence of several shape isomers for each size. Such shape isomers will be analyzed in some detail, and their possible role in generating multiple ionization potentials will be discussed.

The shapes of ^{3}He clusters are found to be close to spherical in contrast to the well deformed shapes of simple-metal clusters. As a result, the fine structure between major shells exhibited by the simple-metal clusters, namely odd-even alternations and subshell closures, is absent in the size-evolution of the chemical potentials and the second-energy differences associated with ^{3}He$_N$ clusters [2].

Furthermore, we will report on the extension of the SE-SCM studies mentioned above to finite temperatures. Applications of the SE-SCM to barriers and pathways [3] pertaining to fission of charged metal clusters will also be presented.

[1] C. Yannouleas and U. Landman, Phys. Rev. B **51**, 1902 (1995).
[2] C. Yannouleas and U. Landman, Phys. Rev. B (15 September 1996).
[3] C. Yannouleas and U. Landman, J. Phys. Chem. **99**, 14577 (1995);
    C. Yannouleas, R.N. Barnett, and U. Landman, Comments At. Mol. Phys. **31**, 445 (1995).

I-8

Electron dynamics in metal clusters:
Vlasov equation approach

L. Plagne, M. Gross, and C. Guet

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We consider a metal cluster of a few hundred atoms in presence of a strong sudden perturbation. The perturbing field can either be associated with a charged particle passing through the cluster or with a fs laser pulse irradiating it.

Over a timescale of less than about 100 fs, during and after the perturbation, the ions remain inert while the electrons experience a strong excitation that leads to emission into the continuum and to large density fluctuations. Questions at issue are which elementary modes are excited, the rate at which the electron system relaxes towards thermal equlibrium and how the electronic energy will eventually equilibrate with the ionic vibrational modes. The latter point is not considered in the present work.

A tractable description of the electron dynamics which necessarily precludes either a full many-body calculation or a standard perturbative Born-type approximation is conveniently offered by a time-dependent mean-field theory such as the time-dependent Hartree-Fock model (TDHF). However, owing to the large number of electrons involved, solving the TDHF equation remains a heavy task. In the present alternative approach, one solves the Vlasov equation, which is simply the semi-classical limit of the TDHF equation. Although it is a classical equation it still complies with the Pauli exclusion requirement as long as no external field is suddenly added.

We solve the Vlasov equation by combining the test-particle method and the numerical solution of the Poisson equation at each time step. This method allows one to use a huge number (10^6) of test particles and to obtain a reliable behavior of the one-body phase-space density over more than 50 fs.

The method is used to simulate collisions of (multi)charged ions with sodium clusters ($Na_N, N = 20, 300$) at relative velocities around the Fermi velocity. We predict the energy loss of the projectile and the rate and features of the sudden electron emission. Moreover various plasmon multipoles are clearly identified as for instance the compressional mode. Comparison with hydrodynamical models is made.

Structural optimization of atomic clusters using a genetic algorithm*

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Iowa State University,

Ames, Iowa 50011, U.S.A.

We present an efficient method for determining the lowest energy structure of an atomic cluster starting from atomic coordinates chosen at random. The method is based on a genetic algorithm, which operates on a population of candidate structures to produce new candidates with lower energies. Results of applications to carbon clusters (up to C_{60}) and other systems will be presented.

* Work done in collaboration with D. Deaven, J. R. Morris, C. Z. Wang and N. Tit.

Magnetic anisotropy of transition-metal clusters, chains and films

G. M. Pastor

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The magnetic anisotropy energy (MAE) and related electronic properties of $3d$ transition-metal (TM) clusters, chains and films were determined by calculating *self-consistently* the effects of the spin-orbit coupling on the spin-polarized charge distribution and on the electronic spectrum for different orientations of the magnetisation. The MAE shows a complicated, non-perturbative behaviour as a function of relevant external variables such as system structure (cluster size, chain length, film thickness, etc.), inter-atomic bond-length and d-band filling n_d. The easy and hard axes alternate between the off-plane and different in-plane directions in particular as a function of n_d. Thus, transitions between uniaxial- and multiaxial-type of MAE surfaces are identified. In agreement with experiment, we find that the MAE of small clusters is considerably larger than in the corresponding crystals, often even larger than in thin films. Remarkably, the in-plane anisotropy can be of the same order of magnitude as the off-plane anisotropy. The implications of these results are discussed in connexion with cluster-beam Stern-Gerlach experiments. Motivated by the search for materials showing particularly large MAE's, we analyse the rich behaviour of one-dimensional and quasi one-dimensional structures as a function of chain length, chain width and n_d. Finally, the magneto-anisotropic properties of these various low-dimensional systems are contrasted.

Clusters of interest for liquid ionic alloys

J. A. Alonso [1], M. J. López [1], L. M. Molina 1, J. Chang [2] and M.J. Stott[2]

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2. Department of Physics, Queen's University, Kingston, Ontario K7L 3N6, Canada.

The production of an excepcionally abundant an stable intermetallic cluster Na_6Pb has recently been reported. In an attempt to understand this feature we have performed ab initio total energy calculations for clusters Na_nPb with n=3-8. The lowest energy structures and the evaporation energies of these clusters have been determined. The energy to evaporate a Na atom fron Na_6Pb was found to be 1.58 eV, larger than that for bigger clusters. We propose that the high abundance of Na_6Pb results from a cascade of evaporations from larger clusters which becomes blocked at Na_6Pb. We also found that Na_4Pb was particularly stable. In fact the existence of clusters (or complexes) Na_4Pb in liquid Na-Pb alloys is suggested by the behavior of many electronic and thermodynamical properties of those alloys.

In addition, to shed light on the possible formation of complexes in alloys of Pb with alkali metals and their stoichiometry we have performed calculations for sequences of clusters with formula A_mPb_n, where A is an alkali atom (Li - Cs), n = 1 or 4 and m<9. The calculations were performed using an spherical-average approximation for the cluster potential. The total energies suggest that clusters with composition A_4Pb and A_4Pb_4 are very stable against a change in the number of alkali or Pb atoms, and support the possibility of these clusters forming in the liquid alloys. In fact, the experimental data suggest the formation of Li_4Pb and Na_4Pb complexes on one hand, and K_4Pb_4, Rb_4Pb_4, Cs_4Pb_4 on the other.

Structure, Stability and Dynamics of Supported Metal Clusters

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Understanding the interaction of clusters with surfaces has drawn increasing interest within the cluster physics community during the recent years. Knowledge of cluster-surface interaction is crucial for a better control of processes such as deposition of energetic clusters for growing thin films of good quality, or low-energy deposition with soft-landing techniques which opens up new tools to measure fundamental properties of size-selected substrate-supported clusters. While most of the theoretical work done so far is based on atomistic simulations using classical empirical or semiempirical models for the interatomic interactions, proper first-principles quantum-mechanical methods are required to study small metal clusters, the physics of which is known to be governed by their electronic structure.

Here we discuss recent studies[1] aimed at providing insight into basic interactions between small metal (sodium) clusters and chemically inert surfaces such as the (001) surface of NaCl crystal. The calculation method[2] relies on the Kohn-Sham formulation of the density functional theory, *ab initio* pseudopotentials with plane-wave basis sets and the use of Born-Oppenheimer approximation on the separation of the time scales between the electronic and ionic degrees of freedom. We start by discussing the nature of adsorption of a single sodium adatom both on ideal and defected surfaces, followed by discussion on the zero-temperature ground state structures for the smallest adsorbed clusters as well as high-temperature simulations performed to study the stability and dynamic properties of selected clusters. Furthermore, we discuss the electronic structure of the adsorbed clusters by using a simple deformable jellium model embedded in a background potential parametrised to mimic the interaction with the substrate[3].

[1]H. Häkkinen and M. Manninen, Phys. Rev. Lett **76**, 1599 (1996); Europhys. Lett. **34**, 177 (1996); submitted to J. Chem. Phys. (1996).
[2]R. N. Barnett and U. Landman, Phys. Rev. B, **48**, 2081 (1993).
[3]J. Kolehmainen, H. Häkkinen and M. Manninen, submitted to Z. Phys. D (1996).

Small Metal Clusters as Models for Reaction Sites on Surfaces

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Recent experimental studies investigating the spectroscopy, kinetics and dynamics of small metal clusters and metal cluster complexes will be reviewed and their implications for the development of small metal clusters as models for reaction sites on surfaces will be discussed.

Methods for optical control of time dependent processes in clusters and their reactions

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The time dependent laser induced processes in clusters are investigated with the aim to extract the leading physical effects which are responsible for controlled excitation dynamics and for time development of the non-equilibrium states. For this purpose ab–initio density matrix approach has been developed which is suitable to treat the whole manifold of involved excited electronic states simultaneously with the motion of the nuclei. The method allows to treat the intrinsic interactions as well as the coupling to the external fields at the same footing. The time scale for different dynamical correlation effects has been studied. For example the analysis of the time scale as well as of dynamics of localized/delocalized electronic excitations in nonstoichiometric alkali–halides containing excess electrons will be presented.

The investigation of controlled non-equilibrium dynamics on neutral and charged silver clusters has been carried out in order to follow the geometrical relaxation processes. The results serve directly to interpret the experimental investigation of the time evolution of a coherent non-equilibrium state in neutral clusters using femtosecond negative–to neutral–to–positive technique. A complementary direction involving the development of the variational method for calculation of electronic–vibronic Born–Oppenheimer states for determination of the vibrational fine structure will be presented. This approach is applied also to treat vibrational fine structure of different isomers of Ag_5 cluster.

Ultrafast Dynamics of Small Clusters upon Ionization and Photodetachment

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The ultrafast relaxation of small clusters immediately after ionization and photodetachment is studied. For small Hg_n clusters we determine the fragmentation-time distribution induced by ionization. A dramatic change of the fragmentation behavior occurs when the temperature before ionization reaches the melting point of the neutral clusters. This new effect could allow to determine the melting point of small clusters by pump and probe experiments. The ultrafast dynamics depends non-linearly on initial conditions regarding atomic positions and velocities. The resultant largest Lyapunov exponent increases strongly upon ionization. We also determine for Ag_3 the time scale for the change of the linear to a triangular structure after the photodetachment process $Ag_3^- \rightarrow Ag_3$. We show that the time-dependent change of the ionization potential reflects in detail the internal degrees of freedom, in particular coherent and incoherent motion. This is sensitive to the initial temperature. We compare with experiment and point out the general significance of our results.

Atomic Clusters: Building Blocks for a New Class of Solids

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Atomic clusters constitute a new meta-stable form of matter that possesses unusual electronic, magnetic, optical and thermodynamic properties. The large surface to volume ratio as well as the discrete energy level structure are responsible for their unique size-specific properties. It is argued that new materials with novel properties could be synthesized if clusters instead of atoms form the building blocks. The difficulty arises since the clusters have a tendency to coalesce when assembled. Current techniques to prevent this coalescence include coating clusters with surfactants, isolating them into matrices, or depositing them on substrates that limit cluster diffusion. An alternate approach is to design cluster composition in such a way that it renders the clusters unusual stability and chemical inertness. It is hoped that such clusters can be assembled without losing their individual identity. The ideas behind the design of stable clusters and the properties of crystals constructed with these clusters as building blocks will be discussed.

Cluster Theory. What Is New?

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We shall address the current 'state of art' of the understanding of cluster theory, focusing on the following issues:

(1)   The grand unification of structure, electronic level structure-energetics thermodynamics-spectroscopic and dynamic attributes.

(2)   Cluster size effects and dimensionality scaling.

(3)   Electronic level structure.

(4)   Elementary excitations.

(5)   Quantum clusters.

(6)   Nuclear and electronic dynamics.

(7)   The records of ultrafast dynamics.

Roundtable Discussion 1

Cluster Modelling, Calculations, Simulations: the State of the Art in Electronic Structure Calculations into the Next Millenium

Moderator: Dennis Salahub

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Panelists have been chosen to cover a broad range of theoretical and computational approaches applied to a wide variety of cluster applications. Each panelist has been asked to prepare a **very brief** (ideally 5 minutes, 10 max.) opening statement using, at most, two or three overheads that will illustrate **with concrete examples**:

i)   the state of the art for one or more computational techniques
ii)   the kind of important problems that can be solved **now**,
        a) with "typical" computing resources (workstations and servers),
        b) with "untypical" amounts of "supercomputer" or high
        performance computational resources.
iii)   the kind of important problems that one will be able to solve 5 years from now, in 2001.

The audience and the panelists will then be invited to comment on whether the opening statements:

i)   really reflect the state of the art
ii)   have been overly optimistic in their projections
iii)   have been overly pessimisitic in their projections.

TAMC-2 Participants are invited to present **one or (if absolutely essential) two** overheads to support their views on the above questions. **It is planned to devote the majority of the two-hours to open discussion. Please come prepared**!

My own contributions will illustrate the possibilities of Kohn-Sham Density Functional theory, including Born-Oppenheimer Molecular Dynamics, using the deMon suite of computer codes for i) bare and ligated transition-metal clusters, structure and spectroscopy and ii) hydrated proton clusters, simulated annealing, structures, vibrational spectra, dynamics.

WAVEFUNCTION-BASED

AB INITIO MOLECULAR DYNAMICS OF CLUSTERS

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In this roundtable discussion, I will briefly discuss the advantages and disadvantages of using wavefunction-based ab initio molecular dynamics (AIMD) for studying the structure and dynamics of clusters. The main advantages from an MD point of view are that one does not have to assume some arbitrary functional form for the interatomic interaction potential, but rather computes the energies and forces directly from the quantum mechanics. From the electronic structure point of view, the coupling to dynamics allows one to search for minima in an unbiased manner by employing simulated annealing. Examples of structural and dynamical properties predicted from these techniques will be given. Obviously, the main disadvantage is the considerable expense of such techniques, especially compared to variants based on density functional theory. Time permitting, I will discuss a new numerical ab initio electronic structure method we have developed recently that reduces the conventional scaling of Hartree-Fock and Generalized Valence Bond methods to N^3 (asymptotically to N^2), while retaining high accuracy of the forces. In addition to reducing the scaling properties of the method and retaining accurate forces, it is ideally suited for parallel processing, which should allow large systems to be treated with wavefunction-based ab initio MD in the future.

Electronic Structure Calculations For Clusters Within Density Functional Theory

Arne Rosen

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

Calculations within the Density Functional theory covering the following topics will be discussed:

1. Electronic structure for free metal clusters.
2. Use of jellium model for analysis of electronic structure and reactivity of Cu clusters.
3. Electronic structure and optical properties of C_{60}, metal covered C_{60}, nanotubes, nanowires etc.
4. Size dependent melting for clusters.

Density functional study of small transition metal clusters

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In the last few years the interest in the study of small metal clusters has grown considerably. The properties of these systems may show both similarities and differences with respect to their bulk counterparts. Cluster properties depend on the number of atoms expecially in small clusters, and they can sometimes change dramatically whene one atom is added to or removed from the cluster. The electronic structure of transition metal clusters is particularly complicated because they include atoms with both relatively localized nd (n=3,4,5) and relatively delocalized (n+1)s electrons. From a theoretical point of view, the correlated post-Hartree-Fock or the density functional methods, can give extensive information on spectroscopic constants and reaction mechanisms for many elements. For metals, reliable computations require the treatment of electron correlation that increases significantly the computational effort in HF based methods. Recently, the development of density functional methods and related computer codes has changed this situation considerably. Now reliable calculations are possible also for small clusters of transition elements at relatively low computational cost.

Linear Combination of Gaussian-Type Orbitals Density Functional Theory (LCGTO-DFT) computations have been performed for:

- Al_n $(n \leq 5)$, $Al_n^+(n \leq 5)$, Al_n^- $(n \leq 5)$;
- Cu_n $(n \leq 5)$, Cu_n^+ $(n \leq 5)$, Cu_n^- $(n \leq 5)$;
- Sc_n, Y_n $(n \leq 4)$
- X_3 (X= Cr, V)
- Al_nO, Al_nO_2 $(n \leq 4)$

Equilibrium geometries, harmonic frequencies, adiabatic and vertical ionization potentials, electron affinities and binding energies have been computed. Results are compared with the available experimental and previous high level theoretical data.

Roundtable Discussion 2

Landscapes of Potential Energy Surfaces: Analyses and Consequences for Dynamics

Moderator: R. Stephen Berry

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Advances in computational tools, analytic methods and physical insight have made possible new levels of insight into the topographies of potential surfaces of complex systems containing many particles, and into the dynamics driven by these topographies. Large clusters of atoms and of molecules, and foldable proteins are just such complex systems. This session will explore the current state of understanding, for atomic clusters, for water and for proteins, of the chain of concepts from interparticle forces to topographies of multidimensional potential surfaces to dynamics on such surfaces to nucleation and growth to formation of glasses or of highly specific structures.

Fluctuation, Relaxation of Water Cluster; Non-Statistical Dynamical Behavior, Proton Transfer, Evaporation and Relaxation

Iwao Ohmine

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<u>Relaxation phenomena in model</u> $(H_2O)_{20}$ <u>clusters</u> are investigated by considering energy fluctuations and dielectric relaxation, making connections with the underlying hydrogen-bond rearrangement dynamics. In particular, we relate these effects to the potential energy surface, including rearrangement mechanisms, minimum energy pathways and normal mode excitations. The statistical behavior of the structure transition in the water cluster is examined. The transition rate estimated from the statistical theory (RRKM theory) is compared with that obtained by the molecular dynamics (MD) simulation. The RRKM rate is 1-3 order of magnitude larger than MD value. Their difference is larger in the low energy. To find an origin of this discrepancy, the mechanism of coupling among various modes is examined. It is found that there is coupling among only a subset of normal modes, not entire modes, in a low energy dynamics. The modified statistical (RRK) theory, assuming that only a sub set of modes contribute to the reaction rate, well reproduces the energy dependence of the MD transition rate. It is also found that the energy fluctuations and dielectric relaxation are non-Debye in character, but instead exhibit so-called 1/f spectra.

 <u>A proton attachment dynamics to a water cluster</u> is investigated by using a classical molecular dynamics calculation. It is found that three dynamical stages are involved; (1) ultrafast ($\sim 10^{-14}$ sec) proton attachment to a water molecule of the cluster which followed by (2) the fast ($\sim 10^{-13}$ sec) sequential proton transfer over several water molecules on the cluster surface and then (3) the gradual ($\sim 10^{-11}$ sec) proton penetration to the cluster core. In the first two stages, the large kinetic energy of the order of hundreds kcal/mol is released to the system, which results in the evaporation of a few water molecules from the cluster. The water molecules evaporating in these early stages have large vibrational and translational energies. The mechanism of the energy relaxation and the proton transfer in each process are investigated. The large amplitude vibrational motion promotes sequential concerted proton exchange transfers in the earlier stages (1) and (2) The precise configurational matching of the hydrogen bond coordination and the O-O distance fluctuation is the most important factors to determine the direction and the rate of the proton transfer in the stage (3).

Protein Folding Funnels: Exploring the Energy Landscape.

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Globally the energy landscape of a folding protein resembles a partially rough funnel. The local roughness of the funnel reflects transient trapping of the protein configurations in local free energy minima. The overall funnel shape of the landscape, superimposed on this roughness, arises because the interactions present in the native structure of natural proteins conflict with each other much less than expected if there were no constraints of evolutionary design to achieve reliable and relatively fast folding. This funnel shape is necessary to overcome the Levinthal paradox, i.e., the unlikely possibility of proteins finding a unique stable folded conformation by random searches. Particularly at this Symposium, it is interesting to notice the connection between protein folding funnels and the topography of the landscape of other systems seeking specific structures. In recent papers, Berry, Wales and collaborators have shown a funnel-like topography for the KCl_{32} cluster that, as stated by them, is similar to the landscape of folding proteins.

In the spirit of the physics of phase transitions, experimental information on the structure and dynamics of the molten globule can be used to find the global characteristics of this funnel energy landscape for the folding of small helical proteins (around 60 amino-acids) when supplemented by a simple theory of the helix coil transition in collapsed heteropolymers. These results allow us to establish a law of corresponding states which relate simulations on "minimallist" lattice models to real proteins which possess many more degrees of freedom. This model predicts a transition state located midway between the folded and unfolded states that is composed of an ensemble of delocalized nuclei. Several recent experiments lend support to these predictions. We will discuss our recent work using "minimallist" lattice models. The advantage of these models is that they can be studied in great detail so one can determine how the various factors affect folding, both kinetically and thermodynamically. We will conclude with a quantitative description of protein folding kinetics using a diffusive collective reaction coordinate. Folding in this system is best seen as a diffusive, funnel-like process.

Global Analysis of Potential Energy Surfaces

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To understand the structure, dynamics and thermodynamics of a molecule or cluster it is generally necessary to have some sort of global view of the underlying potential energy surface. For some smaller systems a complete catalogue of the minima and transition states is possible, providing very detailed insight into their behaviour. The advent of far-infrared vibration-rotation-tunneling spectroscopy has produced spectra for small water clusters which present a new challenge to theory. To interpret the tunneling splittings in these spectra requires detailed calculations of rearrangement pathways and consideration of a complete reaction graph for the feasible mechanisms.

It is neither possible nor necessary to produce such exhaustive lists for larger systems. However, a representative sample of stationary points can still produce considerable insight into both dynamics and thermodynamics. Model partition functions constructed using the superposition approximation and combined with appropriate order parameters enable us to visualise the contributions of different regions of the potential energy surface to thermodynamic functions. Insight into dynamics and the 'funneling' properties of a surface can be gained by constructing sequences of rearrangement pathways. It is also possible to use a master equation approach to solve the dynamics of realistic model surfaces essentially exactly. Using this technique we have recently been able to draw some quite definite conclusions about the features of a potential energy surface required for efficient 'funneling'. Such a surface has low barriers, a single funnel and a steep potential energy gradient.

Contributed Talks

Clusters In Nanowires And Nanostructures

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Clusters may occur in different environments and states of aggregation; in the gas-phase, supported on surfaces, and in two- and three-dimensional assemblies. In this talk, we focus on two systems: (i) a sodium nanowire characterized by an one-atom contact [1], and (ii) passivated gold clusters adsorbed on graphite and assembled into 3D superlattices [2]. Using ab-initio local-spin-density functional simulations, we show that the structure at the apex of an one-atom-contact sodium nanowire resembles that of a corresponding isolated sodium cluster, and analyze the electrical conductance and dynamical fluctuations in the wire. Structure, morphology, thermodynamics, and dynamics of thiol-passivated gold clusters will be discussed for various states of aggregation, including highly-mobile clusters on a graphite surface, and 3D superlattices whose structures depend on the chain-lengths of the passivating molecules and on temperature.

[1] U. Landman, R.N. Barnett, and W.D. Luedtke, Z. Phys. D (1996).

[2] W.D. Luedtke and U. Landman, J. Phys. Chem. (8 August 1996); Adv. Mater. 8, 428 (1996).

Ionization energies, stability and fragmentation dynamics of fullerene ions

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Abstract

The authors present new results from theoretical investigations for ionization energies of fullerenes and molecular dynamics simulations combined with Density Functional methods (Quantum Molecular Dynamics - QMD) of highly charged fullerene ions.

Clusters over a wide size range ($C_{20} \ldots C_{240}$) with positive charges from one up to twenty were investigated. The size and charge dependence of the ionization energies and stabilities are discussed in detail. QMD simulations for the fragmentation of C_{60}^{m+} clusters are presented. The results are discussed in relation to recent experimental results on the fragmentation of highly charged fullerenes. It is shown that C_{60}^{m+} clusters with $m > 16$ explode within a time less than 1 ps into small fragments with up to seven atoms per fragment. Interestingly, during that fast fragmentation process some structural formation takes place, leading to an even-odd pattern of the final mass distribution.

In contrast to the explosion-like fragmentation of the very high charged clusters, the fragmentation of less charged clusters is discussed also.

FRAGMENTATION OF SMALL NICKEL CLUSTERS: DYNAMICAL SIMULATIONS AND STATISTICAL MODELS†

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Collisionless fragmentation of thermally excited Ni_n (n=12-14 and 55) clusters is studied using isoergic molecular dynamics simulations and statistical approaches. A many-body Gupta-like potential is used to mimic the interaction between the atoms in the clusters. The dynamics of the fragmentation process is analyzed in terms of characteristic quantities such as the distance between the centers of mass of the fragments, their relative translational energy, and their interaction energy, all considered as a function of time. Fragmentation patterns (distributions of the fragmentation channel probabilities) and global and channel-specific fragmentation rate constants are calculated as functions of the excess energy and of the size of the clusters. The preferred channel of fragmentation is evaporation of a single atom. This result is in agreement with the available experimental data. Partitioning of the energy between the rotational, vibrational and relative translational motions of the fragments is analyzed. Results obtained from the dynamical simulations are compared with those following from the RRK and TST statistical models.

Ab Initio Monte Carlo: Application To Li$_8$[†]

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An ab initio Monte Carlo scheme has been developed and implemented to investigate structural and thermal properties of clusters. Results of application of this scheme to Li$_8$, including the description of the stages in the solid-to-liquid-like transition of the cluster induced by increasing its temperature, are described qualitatively and quantitatively.

The Motion of Protons in Water-Ammonia Clusters

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The dynamics of clusters $(H_2O)_nH^+$ (n=1,2,3,4) interacting with an NH_3 molecule has been studied by first-principles Born-Oppenheimer molecular dynamics (BOMD) simulations. These small clusters are chosen as prototype systems for studying the mechanisms of proton transfer at atomistic level. We focus on the fundamental steps of proton motion in molecular clusters, the dynamical consequences of proton affinities, and the interplay between proton motion and proton affinity in these systems. A characteristic feature of the motion, the forming and breaking of O-H bonds in H_3O^+, is analyzed in detail. The transfer process is found to be consecutive along a quasi-one-dimensional channel. The umbrella mode in NH_3 can easily be excited to direct the lone-pair of the ammonia molecule to the water clusters. The hydronium ion, however, reorients mainly via rotation. When NH_3 reaches one terminal water molecule of a protonated water cluster, the system undergoes a series of intermediate states in which the mobile protons travel within the water clusters. H_3O^+ transients are formed as protons approach individual water molecules. The lifetime of the H3O+ transient is 8-20 fs, or 1-3 vibrational periods of the O-H stretch mode. Proton transfer is observed for n=1, 2, 3, although for n=3, NH_4^+ $(H_2O)_3$ is in existence with $NH_3(H_2O)_2H^+$. For n=4, $NH_3(H_2O)_4H^+$ is the dominant statistical configuration.

The vibrational spectrum of $NH_3(H_2O)_4H^+$ is analyzed in detail. The features of the spectrum can be used, in principle, to probe the proton motion in the transition state region reactions. In these calculations, the electronic charge distribution is calculated concurrently with the nuclear dynamics. An analysis of iso-charge density surfaces gives qualitative and quantitative descriptions of the dynamics of electronic redistribution. The BOMD is performed in the framework of density functional theory (DFT) with local spin density and generalized gradient approximations (LSD-GGA).

Density Functional-based Raman and IR Spectra of Si clusters

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We have used a new density-functional-based procedure[1,2] to compute the Raman activities and IR strengths of vibrational modes for a variety of Si clusters, including small clusters (N=3-10) for which the cluster structures are reasonably well-known, as well as larger clusters (N=13,20 and 21) for which the structures are still in question. In addition, we present results for a novel Si-based endohedral fullerene system, Zr@Si[20], which was recently proposed.[3]

The computational procedure for obtaining the IR strengths and Raman activities involves first computing the vibrational spectrum of the cluster. We construct the Hessian matrix cluster using finite-differences of atomic forces obtained by systematically displacing the atoms. To get the IR and Raman data, we perform a total of 12 additional self-consistent calculations (independent of cluster size) with assumed external electric fields. From the results of these calculations, we determine the vibrationally induced changes of the dipole moment and polarizability tensor of the cluster, which gives directly the IR intensities and Raman scattering activities.

The results for the small Si clusters are in very good agreement with previous quantum chemical calculations of Raghavachari[4]. For the larger clusters, we provide predicted IR and Raman spectra for various low-energy cluster structures of Si_{13}, Si_{20} and Si_{21}. These should be useful in determining the structure of experimentally observed clusters at these sizes.

[1] D. Porezag and M.R. Pederson, Submitted to PRB.
[2] M.R. Pederson, D. Porezag, K.A. Jackson, Z. Hajnal and Th. Frauenheim, To appear in PRB (15-July 1996).
[3] K.A. Jackson and B. Nellermoe, Chem. Phys. Lett. **254**, 249 (1996).
[4] E. Honea, et al., Nature **366**, 42 (1993); S. Li, et al., Chem. Phys. Lett. **243**, 275 (1995).

Isomers of C_{20}: Is there a reliable theory?

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The energy ordering of the isomers of C_{20}, the smallest carbon cluster which can exist as a fullerene cage, has been a notoriously difficult problem to describe theoretically. The cage, bowl, and ring isomers have been studied previously by many different theoretical techniques and yield widely different relative energies, sometimes differing by as much as 100 kcal/mol or more. In particular, several different popularly used gradient corrected density functional methods yield different isomer energy orderings.

In this work, the origin of the difficulty of theoretical methods to describe the isomers of C_{20} is explored. New schemes are proposed to calculate the relative energies of the isomers reliably. In particular, isodesmic reactions (where the chemical bond types are similar on both sides of a reaction) are studied from which the heats of formation of the different isomers can be obtained from the known heats of formation of smaller hydrocarbons. Comparisons are made with the known experimental observations and implications of our results to fullerene growth mechanisms are pointed out.

Structural and vibrational analysis of amorphous Au$_{55}$ clusters*

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We present a structural and vibrational analysis of several amorphous (disordered) and ordered isomers of a 55-atom gold cluster. A Gupta n-body potential, with parameters fitted to gold clusters, was used to model the metallic bonding in the Au$_{55}$ cluster. Molecular dynamics method combined with simulated annealing and quenching techniques were used to perform the cluster structure optimization. Our results show that several non-equivalent and nearly degenerate in energy amorphous cluster structures are more stable than those with high symmetry like the 55-atom Mackay icosahedron and the fcc cuboctahedron. The calculated distribution of normal frequencies clearly discriminate between amorphous and ordered cluster configurations and confirm their stability. A common neighbor analysis was implemented to characterize the disordered cluster structures, identifying the short-range order of the amorphous phase, according to the local environment of each atom pair in the cluster. Distorted multilayer icosahedral order was found to be the more representative of the amorphous clusters with the lowest energies. At higher energies, the amorphous structures are characterized by the presence of distorted local icosahedral order. The origin of the higher stability of amorphous vs. ordered isomers in Au$_{55}$ is in the short range of the n-body interaction existing in the metal cluster bonding.

Recent Developments in the Theory of Magnetism of Clusters

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Physics Department

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Almost fifty years ago, Stoner and Wohlfarth proposed a classical theory of Magnetism in small particles. The theory was based on several premises and has provided the basic framework for understanding most magnetic phenomenon in small sizes. Recent developments in free clusters and nanoscale particles are however showing new features that violate several premises of this model and provide laboratories for observing new dynamic phenomenon. The talk will review some of these developments.

The talk will begin with a discussion of Ni_n clusters. It will be shown that the magnetic moment changes discontinuously with size and the highs and lows are related to the detailed electronic features. The observed magnetic behavior is consistent with a model of random orientation of cluster moments. The talk will then focus on the strange behavior of Gd_n clusters. A Gd_2 molecule has the highest spin moment per atom and the bulk Gd has a moment of 7.5 bohr magneton per atom. Yet, small Gd clusters have been found to have moments per atom of only about 3.0 bohr magneton per atom. It will be shown that this unconventional behavior is not associated to any electronic pairing but rooted in an entirely different mechanism where competing ferromagnetic and anti-ferromagnetic interactions lead to canted spin configurations. Their implications on the dynamics will be discussed. Finally, the talk will briefly review some very recent results on chains of nano-particles and conclude with an outline of a more modern theory of magnetism in reduced sizes.

FROM ICOSAHEDRAL CLUSTERS TO POLYMERIC FULLERENES

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We have applied a density-functional based nonorthogonal tight-binding (DF-TB) method to study the structure and energetics of different $[C_{60}]_N$-oligomers (N=2, 3, 4 and 5). The applicability of the scheme for finding the ground state of finite clusters, especially of those with icosahedral symmetry was carefully checked against more sophisticated methods including an all-electron, self-consistent (SCF) scheme based on the local-density-approximation (LDA), and the recently developed generalized-gradient approximation (GGA). We find the DF-TB method suitable for calculating accurately the ground state properties and energetics of single shell fullerenes (bucky balls), multiple shell fullerenes (bucky onions), capped fullerene tubes, and tetrahedrally bonded icosahedral clusters.

The DF-TB method then is used to study the vibrational properties of the considered oligomers. To compare our results with the experimental spectra, intensities for each structure have been calculated using the bond polarization model. The theoretically predicted Raman spectra recently by *Burger, et al. Phys. Rev. B, in print,* have been used for an identification of the most probable stable subunits in photopolymerized C_{60} at 380 K and 300K, the dimers and various trimers, respectively. For the C_{60} dimer, the cohesive energy and the frequency of the Raman-active interball mode have also been investigated with an all-electron, self-consistent scheme based on the local-density-approximation (LDA) and the recently developed generalized-gradient approximation (GGA). To address the energetics associated with polymer stability, we have calculated the DF-TB reaction barrier for the dissociation of the C_{60} dimer along two different paths.

As a heteronuclear dimer linkage we proof the stability of $C_{120}O$ and $C_{120}NH$ in support of recent experiments by *Lebedkin et al. Tetrahedron Lett.* **36** *(1995) 4971,* and compare the behaviour of these systems with well known related organic molecules.

Cluster-Surface-Collision: The Influence of Surface Orientation, Cluster Size, and Electron-Phonon Coupling

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The impact of Cu_{1000}, Cu_{2000}, and Cu_{3000} clusters with 10 keV kinetic energy onto low index copper surfaces was simulated by Langevin molecular dynamics. An embedded atom method potential was used to calculate the trajectories of up to 400 000 atoms for 50 ps. The microscopic evolution is visualized by macroscopic, local quantities, like density, temperature, pressure, or velocity. The standard definition of these fields has been generalized for processes on the submicron scale, replacing the average of a physical quantity over the atoms in a limited volume element by a moving average. A generalized local temperature and pressure can thus be defined. The local density was calculated by smearing out the nuclear mass over a finite region.

The evaluation of vector velocity plots for the impact of the Cu_{1000} cluster provides a clear picture: the cluster penetrates the surface and generates a plastic flow, which depends strongly on the surface orientation. The atoms prefer to move in the (110) and (111) direction, as expected from elastic theory. The shear anisotropy of copper is responsible for the decreased mass transport along the (100) direction. The evolution of a shock wave with about 70 GPa peak pressure is studied by observing the density and the pressure fields. The anisotropy of the crystal's sound velocity causes a dependence of the shape of the shock wave on surface orientation. Surface and cluster atoms are ejected in the first stage of the collision. An enhanced sputtering is observed for the Cu(111) surface. Interstitials, vacancies and dislocations are formed near the point of contact. The cluster and the surface are heated owing to the strong compression. Temperatures of several thousand Kelvin indicate local melting. After 50 ps the system has cooled down to room temperature. Because of the anisotropy in mass transport, the final shape of the surface depends also on surface orientation. The (100)- and the (110)-surface showed a crater with a circular or a elliptical rim, respectively. On the (111)-surface a much flater crater is formed.

At constant energy, the size of the cluster has no significant influence on the dynamics of the impact. The only effect of increasing the cluster size is a flattening of the crater, as a consequence of the larger mass deposition. For the impact of a Cu_{3000} cluster no crater remains, because it is completely filled.

In order to evaluate the importance of the electron-phonon coupling, the electronic energy loss has been incorporated in a reference calculation by an additional damping force. As it had no significant influence on the results, it was neglected in the other calculations.

Electronic and magnetic properties in mesoscopic tubule and permanent current

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Finite length mesoscopic carbon nanotube are investigated with the Hubbard Hamiltonian :

$$H = \sum \varepsilon(h) \, c_h^+ \, c_h + \sum_i U \, n_{i\uparrow} \, n_{i\downarrow}$$

where the energy spectra $\varepsilon(h)$ has been derived from a tight binding calculation involving σ and π electrons.

In a first part, the consequences of the intraatomic correlation term U on the electronic and magnetic properties in mesoscopic nanotubule $B(0,1)n$ (n is the number of hexagons on the circumference) are examined with the Gutzwiller approach. In particular the critical U to obtain (anti)ferromagnetism is derived versus n.

In a second part, the disorder is introduced in the finite length tubule, the dependence of the permanent current in the mesoscopic system is studied versus the magnetic flux and the tubule radius.

Packing Transitions in the Growth of Alkali Metal Clusters

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Small metallic clusters form a local geometric configuration quite different from the bulk crystals. As the cluster size increases, several transitions in the local coordination take place before the bulk structure appears. These transitions involve change in the nature of chemical bonds. We have systematically investigated the structural transition of various alkali metal clusters including binary compounds using an *ab initio* molecular dynamics simulation. Among them, Li clusters exhibit unusual transition in their packing pattern. Small lithium clusters ($N \leq 21$) form open structures based on a "solvation shell" which is quite different from other alkali metal clusters. The bonding of these small clusters is partially ionic. Above $N = 25$, a close-packed structure is established based on interpenetrating 13-atom icosahedra. However, the local configuration still differ from that of the bulk crystal. As the size further increases, the ionic nature decreases and the system reaches another close-packed structure based on the Mackay icosahedron at $N = 55$. These growth patterns are consistent with the 9R structure and FCC-HCP polyphases of bulk Li crystal.

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AB INITIO MODEL POTENTIAL FOR MOLECULAR DYNAMICS SIMULATION OF METAL CLUSTERS; APPLICATION TO SILVER HEXAMERS.

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We present an approach to generate a model potential with parameters fitted to ab initio energetic surfaces, calculated by all-electron non-local spin density method. The potential includes two-, three and four-body terms. Each of them consist of an exponential exchange and dispersion terms. The analytical form of the latter was taken from perturbation theory up to the fourth order. The two-step parameter optimization procedure is elaborated. We illustrate the present approach by constructing an ab initio model potential for the Ag6 clusters.

A molecular dynamics (MD) simulation using this potential reveals interesting features in the isomerization of the C_{2v} planar structure (the global minimun on the potential energy surface). The two stages were observed: First, at temperatures around 350 K, the clusters structures fluctuate between two-dimensional (2D) isomers. At higher temperatures (450 K), fast transitions occur between 2D and 3D cluster configurations. For the pentagonal pyramid isomer the transition 3D→2D realized by the apex atom movement towards the pyramid base. The cluster dynamics as a function of its energy up to an evaporation is investigated.

Photoemission spectra and structures of Si and Ge clusters at finite temperature

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We will examine the electronic spectra of small silicon and germanium clusters from first-principles simulations at finite temperature. The calculated spectra yield an accurate description for existing ultraviolet photoelectron data on the negatively charged clusters. The detailed agreement between theoretical and experimental features and the high sensitivity of the electronic spectra to the cluster geometry are exploited to identify the relevant isomers. Our results show the importance of atomic relaxation within the charged cluster, as opposed to photoemission-induced relaxation effects, in determining the observed spectra.

Posters

Vibrational wavefunctions, energy levels and spectroscopy of large clusters: $(Ar)_{13}$ and $(H_2O)_{n=2-5}$

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Calculation of vibrational wavefunctions and energy levels of several types of large anharmonic clusters were reported. Vibrational Self-Consistent Field approximation is used, which employs a mean-field approach to treat the anharmonic coupling between modes. For some of the systems, correlation corrections were introduced to further improve the methodology. Some of the main findings are: 1) The anharmonicity due to coupling between modes plays a far greater role in the vibrational dynamics of clusters than the intrinsic anharmonicity of individual mode. 2) The correlation correction via Perturbation Theory/VSCF calculations have shown that the relative error of VSCF becomes smaller as the size of the cluster increases. The implication is that the mean-field approximation becomes better as a size of the cluster increases and that the application of VSCF calculation to larger molecules becomes even more attractive. 3) Interesting patterns of blue and red shifts of fundamental frequencies were observed and insight into their origin is gained. Overall, the sensitivity and the usefulness of the VSCF method to study the large anharmonic clusters were demonstrated.

Time-Dependent Quantum Simulations of $Li(Ne)_N$ Clusters : Electronic Ground State Properties and Photoexcitation Dynamics

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Abstract

The quantum dynamics of a Li atom in a large Ne cluster were investigated both in the ground electronic state and in excited states of $Li(Ne)_{17}$. Several different classical structures were found for the electronic ground state, and the properties of two of the isomers were studied in detail. The simulations for the electronic ground state were carried out by the Semiclassical Molecular Dynamics (SMD) method, which is most suitable for system at very low temperatures. We found interesting results:

- (a) The atom-atom pair distribution functions show very pronounced quantum effects.

- (b) The SMD frequencies differ considerably from those calculated from classical Molecular Dynamics.

- (c) The two isomers have considerably different vibrational spectra.

The dynamics of photoexcitation were studied by the Classically-based Separable Potential (CSP) method. This method offers a very accurate quantum description of the time evolution for ultrafast process. We found that The dynamics of excitation into Σ and Π electronic states differ greatly. In addition, the electronic excitation spectrum for the different isomers is approximately the same and comparable with the experimental spectrum. This study demonstrates the power of new time-dependent quantum simulation methods in describing the dynamics of large system.

Quantum Dynamics and Raman Spectroscopy of Photoexcited I_2(B) in Large Argon and Xenon Clusters

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Abstract

The early quantum dynamics following the $B(^3\Pi_{0u^+}) \leftarrow X$ photoexcitation of I_2 in large rare gas clusters is studied and the resonance Raman spectrum of these systems is calculated by a novel time-dependent quantum mechanical simulation approach. The method used is the Classically-Based Separable Potential (CSP) approximation [1], in which classical Molecular Dynamics simulations are used in a first step to determine an effective time-dependent separable potential for each mode, then followed by quantum wavepacket calculations using these potentials. In the simulations for $I_2(Ar)_n$ and $I_2(Xe)_n$, with n=17,47, all the modes are treated quantum mechanically. The Raman overtone intensities are computed from the multidimensional time-dependent wavepacket for each system, and the results are compared with experimental data on I_2 in Ar matrices and in liquid Xe. The main findings include: i) Due to wavepacket dephasing effects the Raman spectra are determined well before the iodine atoms hit the rare gas 'wall' at about 80 fs after photoexcitation. ii) No recurrencies are found in the correlation functions for $I_2(Ar)_n$. A very weak recurrence event is found for $I_2(Xe)_n$. iii) The simulations for $I_2(Ar)_{17}$ (first solvation layer) and for $I_2(Ar)_{47}$ (second solvation shell) show differences corresponding to moderate cluster size effects on the Raman spectra. iv) It is estimated that coupling to the $B"(^1\Pi_{1u})$ state or to the $a(1g)$ state have a small effect on the Raman intensities. v) For $I_2(Ar)_{47}$, the results are in very good quantitative agreement with I_2/Ar matrix experiments [2]. The $I_2(Xe)_n$ results are in qualitative agreement with experiments on I_2 in liquid Xe [3]. The reported calculations represent a first modeling of resonance Raman spectra by quantum dynamical simulations that include all degrees of freedom in large systems, and they demonstrate the power of the CSP method in this respect.

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Quantum Dynamics of Photodissociation of Hydrogen Halides Embedded in Icosahedral Clusters and Matrices of Rare Gas Atoms

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Photochemical processes in inert gas environment have been subject to intense experimental and theoretical investigations in recent years, both in in clusters[1,2] and in matrices[3] of rare gas atoms. In the present work we study the photodissociation of HF and HCl molecules in the center of icosahedral $HClAr_n$ ($n = 12, 54, \ldots$) clusters and in a substitutional site in a cubic face centered (fcc) argon crystal.

In order to describe the short time-scale quantum dynamics of the light photofragment, we solve the three dimensional time-dependent Schrödinger equation in a (numerically) exact way whereas the heavy atoms are treated as classical particles. The coupling of the H-atom wavepacket motion to the heavy atom dynamics is modelled by a self–consistent scheme.[4,5]

Apart from the methodological aspect of developing an efficient and quantitative theoretical tool for the description of fast quantum dynamical processes in solvents, the principal motivation for this computational study is to model the cage exit process. Exit probabilities as well as photofragment mobilities are compared for the two systems. Special emphasis will be on the dependence of the dissociation dynamics on the initial quantum state of the HF/ HCl molecule. Analogously to the idea of controlling the yield of photodissociation by vibrational preexcitation,[6,7] the present work examines the possibility of control by selection of rotational states. Previous calculations showed interesting orientational effects of rotational wave functions of matrix–isolated molecules thus opening the way for a "rotationally mediated chemistry".[8]

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THE BAND SHIFT ANALYSIS FOR DIATOMIC IN THE CLUSTERS WITH BENZENE IN NITROGEN MATRIX

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Interaction energy values in the cluster X_2-C_6H_6 (X=Cl, Br) trapped in the nitrogen matrix are found by pair-wise addition method. The band shift (BS) values of intramolecular vibrational transition in a diatomic X_2 were calculated numerically in the manner given in [1]. Spectra were recorded previously by Nelander at 20 K [2].

The feature of this study is related to the estimation of the distributed (local) multipole electric moments of a diatomic X_2. They are fitted to meet an agreement between the electrostatic interactions expressed via local and central moments at long range distances. The method was checked for N_2 and F_2 as test molecules: the electrostatic interaction expansion expressed via thus obtained dipole and quadrupole moments coincides with the electrostatic interaction expressed via *ab initio* local moments (up to hexadecapole) at van-der-Waals (vdW) range distances. An advantage of electrostatic model of benzene presented via distributed charges was found as compared to the distributed quadrupoles (or dipoles and quadrupoles) model.

Polarizability anisotropy of carbon atom, the intercombination rules for dispersive coefficients, terms number of the $C_n R^{-n}$-expression were varied to estimate their influence on the dispersive interaction. Two alternative repulsive potentials (Buckingham-Fowler penalty function and inverse twelfth power one-center potential for each of two interacting anisotropic particles) were used. The first case leads to the underestimated BS value. The second repulsive function permits to obtain qualitative agreement between calculated (-15.2 for Br_2 and -24.2 cm^{-1} for Cl_2) and experimental (-15.0 and -24.9, respectively) BS.

Electrostatic, dispersive and repulsive interactions between cluster's diatomic and closest neighboring matrix molecules were taken into account. Matrix influence was simulated by semi-sphere of the nitrogen molecules which have spatial positions (in any orientations) corresponding to solid α-N_2 phase. We neglected any matrix influence on the X_2 and benzene characteristics. In both cases (Br_2 and Cl_2) the contribution of the interaction with matrix to the total BS values is small as compared to the contribution attributed to the interaction with benzene molecule.

Higher BS value in the Cl_2 case than in the Br_2 one is assigned to smaller vdW radius of Cl_2 molecule. The coincidence between the calculated and experimental BS values corresponds to higher anisotropy of spatial model of Br_2 molecule as compared to respective one for Cl_2 molecule. A possibility of the estimates of the total interaction X_2-C_6H_6 values basing on the "Interaction energy - BS" dependences found is discussed.

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INSTANTANEOUS NORMAL MODE SPECTRA OF QUANTUM CLUSTERS

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We study the spectrum of instantaneous normal mode (INM) frequencies of quantal Lennard-Jones clusters, LJ_{13}, as a function of particle mass in order to understand the dynamical changes associated with the increasing quantum delocalization. Configurations are sampled from the finite temperature equilibrium distribution by a Fourier path integral Monte Carlo procedure. The Hessian matrix at each configuration is diagonalized in order to obtain the quantum INM spectra. For the masses and temperatures in our study, identical particle exchange is unimportant.

Quantum delocalization effects are shown to induce a cluster solid-liquid transition (CSLT), analogous to the thermal melting transition, at a de Boer parameter value of about 0.19 [1]. The de Boer parameter, Λ, is an index of the degree of quantum delocalization and is defined as $\Lambda = \hbar/\sigma\sqrt{m\epsilon}$ where σ, ϵ are the LJ parameters and m is the particle mass. The INM spectra show characteristic changes with increasing Λ including enhancement of the fraction of imaginary frequencies and the development of a slowly decaying high frequency tail. This increase in the fraction of imaginary frequencies stems from enhanced sampling of low-frequency anharmonic regions, since imaginary INM frequencies are related to positive Lyapunov exponents, which increase at the melting transition [2]. The overall force constant for the cluster decreases significantly in the region of the CSLT since the high proportion of barrier crossing motions in the liquid-like cluster results in decreasing cluster rigidity. The Einstein frequency which is the average vibrational frequency associated with the cluster shows a maximum at parameter values associated with onset of cluster melting. Thus the INM spectra can provide useful dynamical information on quantum many-body systems. We expect that the methodology used to extract such quantum INM spectra will prove very useful in defining quantum analogues of classical dynamical quantities in the future.

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A Method for Projecting the Spatial Distribution of Higly Symmetrical Molecules onto a Two Dimensional Surface

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A new method for projecting the spatial orientation of molecules, arranged in a cluster, onto a two dimensional surface is presented. The method is specifically useful to monitor the structural changes of the cluster for the case of highly symmetrical molecules (tetrahedral, octahedral). We have applied it in the analysis of the phase changes of the molecular clusters of tellurium hexafluoride. The configurations of the molecules are obtained by a constant energy MD simulations of the thermal history of free plastic (orientationally disordered) clusters. In these clusters, the molecules are reorienting in a complicated way that depends upon the asymmetry of the molecular interaction. A structural phase change from a more disordered to a more ordered structural phase change from a more disordered to a more ordered phase shows itself as the appearance of a critical number of molecules aligning along a particular rotational axis. The distribution of the molecular rotational axis gives a clear evidence for structural transformations.

CHAOTIC BEHAVIOR IN THREE-ATOMIC CLUSTERS

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Chaotic Behaviors in three-atomic clusters under the influence of Lennard-Jones two-body and Axilrod Teller three-body potential have been investigated. Lyapunov Exponents are calculated to measure degree of chaos for rotating and nonrotating clusters. The strength of three-body interactions is controlled by a reduced parameter, Z, whose value change between 0 and 1. Obviously, the relative magnitudes of two and three-body forces do not remain constant during the integration time, they change according to instantaneous geometry of cluster. The limiting values of the angular part of the Axilrod-Teller potential are -2 and 11/8 (reduced units) for linear and equilateral triangle consecutively. This initial partitioning of the potential energy into two and three-particle interactions seems to play an important role in the measure of chaotic behavior.

THE STRUCTURE OF PHASE SPACE OF ROTATING NOBLE GAS TRIMERS

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The phase space structure of rotating noble gas trimers is investigated by molecular dynamics. Maximal Lyapunov exponent, autocorrelation function of atom momentum on the axis at right angle to the total angular momentum M, and the distribution functions of the interatomic distances are calculated for the trajectories on the energetic hypersurface E=-1.5 at various M. Partition of the phase space on the regions of regular and chaotic motion under fixed E and M is found as well as the partition of the chaotic component on the three ones, differing in the value of the maximal Lyapunov exponent and the shape of autocorrelation function. On the Figure, the dependence of the chaotic trajectories fraction on M is shown. Its non-monotonic character can be explained by the regularizing influence of the cluster linear configuration and the "freezing" of the energy in the rotational degrees of freedom when M approaches the maximal value under given energy.
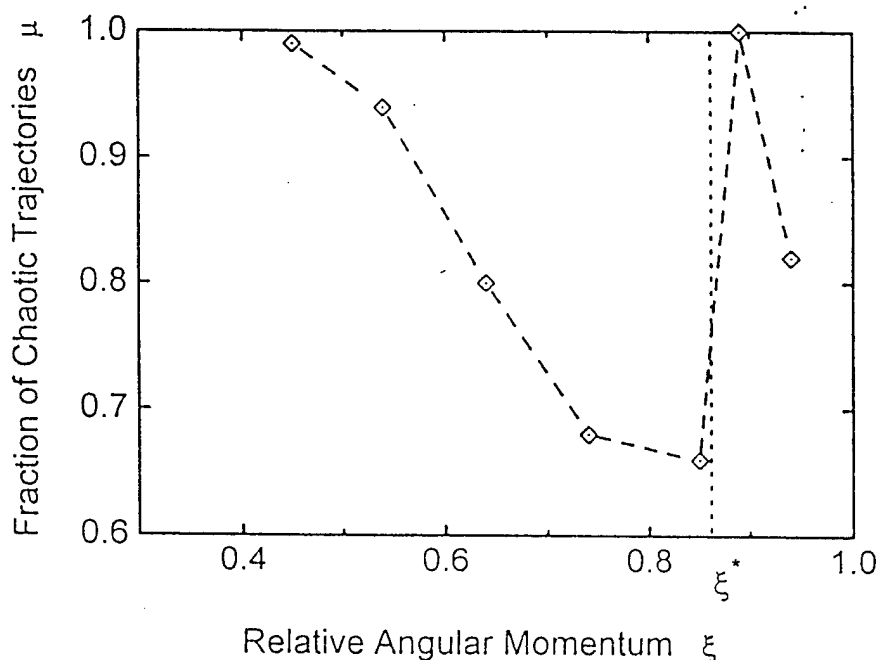
Figure. The dependence of the fraction of chaotic trajectories μ on the trimer relative angular momentum $\xi = M/M_{max}$. Vertical dotted line corresponds to the maximal value $\xi^* = M_{lin}/M_{max}$ for the trimer linear configuration under the given energy E=-1.5.

The dependence of the cluster energy distribution between internal degrees of freedom on the total angular momentum is found.

CONFIGURATIONAL RELAXATION IN CLUSTERS WITH SAWTOOTH AND STAIRCASE POTENTIAL LANDSCAPES

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We have investigated, using molecular dynamics simulations, the isothermal evolution of two clusters, $(KCl)32$ and $Ar55$. These represent two very different kinds of potential topographies, the first a staircase and the second a sawtooth. The potassium chloride cluster was modeled with pairwise Born-Mayer (Coulombic plus short-range exponential repulsive) potentials, and the latter with pairwise Lennard-Jones potentials. Each simulated calculation began with a cluster at a randomly selected but very high-energy point on its potential surface. Both Nose-Hoover (extended system) and stochastic algorithms have been used. The results indicate that the isothermal relaxation process from an initial configuration at a point of high potential energy, after a brief, steep drop in total and potential energy, follows a monotonically decreasing series of well-marked, nearly-constant-mean-energy steps of increasing duration, until the system comes to some 'final' potential basin. The temperature dependence of this final energy and of the rate by which it is reached, has been investigated; one of the conclusions is that the transitions between local potential minima occur from thermally equilibrated states, even on staircase potential. The principal difference in the relaxation of these two clusters is due to difference in their eigen-timescales (different vibrational frequencies) and in the potential topography; the contributions of both of these factors have been examined.

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A Master Equation Approach to Modelling Relaxation on the Complete Potential Energy Surface of $(KCl)_5$

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The potential energy surface (PES) governs the non-equilibrium processes of annealing and isothermal relaxation. Its structure can strongly influence whether the resulting equilibrium state that these processes yield is ordered (crystalline) or disordered (glassy).

As in earlier work,[1-4] the approach taken here is to obtain a representational sample of inherent structures on the PES and the transition states between them. To model the evolution of the system to equilibrium, we employ a stochastic master equation with RRKM-theory transition rates between inherent structures on the PES. As a test to our model, we examine the master equation behavior of $(KCl)_5$, for which the entire PES for bound-state configurations is known, and compare its predictions for the equilibrium probability distributions to the results of constant-temperature molecular dynamics simulations.

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MIXED Ni-Al CLUSTERS:
ISOMERS, HOMOTOPS AND THERMAL BEHAVIOR[†]

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Results of extensive numerical simulation studies of structural and dynamical properties of Ni-Al alloy clusters derived from a many-body potential are presented and discussed. The structural analysis is performed in terms of isomers (geometrically different forms) and homotops (different distributions of the two types of atoms within a given geometry) corresponding to clusters of different stoichiometric compositions. New definitions of mixing energy and mixing coefficient (a quantitative measure of the degree of mixing of the two components), which are applicable not only to pairwise-additive but also to many-body potentials, are given. It is shown that the energy ordering of the manifold of structures can be rationalized by grouping the different structural forms into classes. Each class is defined by isomeric form, stoichiometric composition and the type of the central atom. The energy ordering within each class is governed by the value of the mixing coefficient.

The thermal properties are derived from an analysis of the evolution of the cluster dynamics with the energy. It is shown that the solid-to-liquid-like transition experienced by clusters as their energy is increased may include stages such as isomerizations involving only surface atoms, isomerizations involving all atoms, surface melting and complete melting. The presence (or absence) of each individual stage in the transition of a given cluster depends on its stoichiometric composition. A close correlation between the features of dynamics and the patterns of the energy spectra of the structures is established.

CLUSTER AND NANOWIRE CONTACTS:
STRUCTURAL ANALYSIS AND GROWTH DYNAMICS†

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A structural analysis of atomic-scale cluster and wire contacts between two metallic plates is presented. The interatomic forces, both in the contacts and the plates, are described by a semiempirical many-body potential representing aluminum. The cases of rigid and adjustable plates are considered. Equilibrium geometries and energies of the plate-cluster-plate system are obtained as a function of the separation between the plates.

The dynamics of formation of a nanowire contact from atomic-scale ridges deposited on the plates is described and the possibility of "growing" networks of nanowire contacts from networks of ridges is examined.

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CONDUCTANCE OF A CLUSTER CONTACT:
FIRST PRINCIPLES CALCULATIONS†

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Electrical conductance through a cluster contact between two aluminum plates is calculated as a function of the separation between the plates. The equilibrium configuration of the system, as obtained from a many-body description of the interatomic forces between the constituent atoms, is used for each separation. The shape of the contact is that of two pyramids, each of which contains 13 atoms, connected through a common extra apex atom. The calculations are performed within a scheme that combines the density functional (local density approximation) description of the valence electrons of the atoms in the contact with a pseudopotential representation of the ionic cores of these atoms and the jellium model description of the plates. It is shown that there exists a critical separation between the plates such that for distances equal or larger than this separation the cluster contact "breaks" (reconstructs): the apex atom moves from a symmetrical position between the pyramids closer to one of them. This change in the shape of the contact results in the reduction of the conductance and a transition from the ballistic to tunneling conductance regime.

The issues discussed are of relevance to a broad variety of microelectronic devices, including atomic-scale microscopies and phenomena such as quantization of conductance in nanowires, etc.

Dynamics, stability, and fragmentation of sodium clusters: a semi-classical molecular-dynamics approach

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We present a new semi-classical molecular-dynamics (MD) technique, which we have applied to study structural and dynamical properties of Na clusters in a size range of up to several hundred atoms. In this technique, the classical forces on the Na^+ ions are calculated at each time step from an *ab initio* electronic density computed in the self-consistent extended Thomas-Fermi approximation. We use a Car-Parrinello-like algorithm to ensure an ionic dynamics on the ground-state Born-Oppenheimer surface for this semi-classical approximation of the valence electrons. The method is cheaper than quantum MD approaches and allows us to study systems up to much larger sizes than have previously been reported, at the price of neglecting electronic shell effects, which however have reduced importance as the size of the system increases.

Volume and surface-energy parameters, vertical ionization energies, and r.m.s. ionic radii are extracted from the model and found to agree well with experiment in a smooth liquid-drop sense. We study the radially averaged ionic density, which at 0 K consists of concentric spherical shells. This structure collapses gradually with increasing temperature until for $T > 350$ K the time-averaged density is jellium-like with a diffuse surface. For charged clusters, the time-averaged *net* charge density is found to reside in the surface region of the cluster, consistent with the macroscopic limit of a conducting sphere. The Fourier transform of the velocity autocorrelation function is found to have an upper cut-off at frequencies of order $6 \cdot 10^{12}$ Hz, as for bulk liquid Na, but the behavior at low frequencies is different from the bulk. Low frequency collective ionic quadrupole and octupole oscillations may be identified in a small range of frequencies around the prediction of the incompressible liquid-drop model. A sharp monopole oscillation is also observed at a frequency of order 10^{12} Hz, consistent with a compressible liquid-drop model.

The technique is applied to calculate fission barriers. stability limits, and ionic and electronic deformation shapes during fragmentation processes, within the semi-classical approximation of neglecting shell corrections. We find close agreement with the charged-liquid-drop picture of symmetric fission and critical charge, within this approximation. Asymmetric fission of clusters with subcritical charge is also studied. The peak of the fission barrier here occurs when the two fragments are nearly touching and an electronic "bridge" between them just starts to form.

Preliminary work will also be discussed on dynamical studies of fragmentation and Coulomb explosion for systems containing upwards of 40 atoms, using both the semi-classical MD technique described above as well as an approximate Kohn-Sham MD technique.

Fission of metallic clusters in the Liquid Drop Model with shell correction effects

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Using the Liquid Drop Model, within the Jellium Model, and the Strutinsk shell correction method we calculate fission barrier heights as a function of charge and mass asymmetry, for a family of shapes consisting of two spheres connected by a quadratic surface. We find the fissibility for which a mass asymmetric splitting gives place to the symmetric one (Bussinaro-Gallone point) and evaluate the size of charged clusters of alkali metals for which the fission barrier height is equal to the evaporation energy (critical sizes). The results for the critical sizes agree very well with experiment.

Shell effects are included using the Asymmetric Two Centre Deformed Harmonic Oscillator. We show that shell correction can have a dramatic effect on shaping the fission barriers.

The lifetime of large clusters.

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The lifetime of large clusters with pair interactions of atoms is analyzed. The statistical and liquid drop models are used with the assumption that the cluster decay leads to releasing of one atom. In the statistical model the Kompaneets version of RRKM model is used. In this model the cluster is described as a set of harmonic oscillators with identical frequencies. This usage is possible because the lifetime of a large cluster τ does not depend on oscillator frequencies (one atom is released). It has the form:

$$\tau = t_0 \exp(\varepsilon/T)/n_{sur} \qquad (1)$$

T is the cluster temperature expressed in energetic units, ε is the binding energy of the released atom, n_{sur} is the number of surface atoms, possessing this binding energy, t_0 is a typical time of change of oscillator numbers distribution. The parameter t_0 cannot be determined within the framework of the statistical model, because the assumption of the harmonic character of oscillations is not valid in the transition region. For determination of this parameter we use the liquid drop cluster model that takes into account the connection between rates of evaporation and attachment of atoms when an atomic gas is in equilibrium with a flat surface. Then the evaporation rate is expressed through the atom number density N_{sat} of saturated vapor, which is approximated by formula:

$$N_{sat} = N_0 \exp(-\varepsilon_\infty/T) \qquad (2)$$

ε_∞ is the atom binding energy with a plane macroscopic surface. This model gives the following expression for the lifetime τ of the macroscopic cluster:

$$\frac{1}{\tau} = \sqrt{\frac{T}{2\pi m}} * N_0 a^2 \xi \, n_{sur} \exp(-\varepsilon/T) \qquad (3)$$

m is the atom mass, a - is the distance between nearest neighbors, ξ -is the probability of atom attachment as a result of its contact with the macroscopic surface.
Though the considering models correspond to the different cluster temperatures, their comparison and also comparison with the numerical calculations allow us to correct the analytical expression for the lifetime of large clusters.

STUDY OF METAL-SUPPORT INTERACTION

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ABSTRACT

Small supported metal particles (10-15 A) are now used as catalysts in fine chemistry. The metal-support interaction is thus a non-negligible factor in catalysis. However, this aspect has never been considered in theoretical studies.

As a first step, we have analyzed how one Pd atom binds to the surface of model clusters of MgO. There is no experimental evidence for the binding site of Pd. Oxygen seems more probable from a chemical point of view, but a SEELFS study of Pd clusters on a surface of MgO proposes that Pd atoms are bound to Mg atoms, at a distance of 1.5 A.

MgO clusters of various sizes (from MgO to $Mg_{20}O_{20}$) supporting one Pd atom on top of O, Mg, in bridge or four-fold sites have been studied. In all cases, the binding of Pd with O is favored. and the calculations show that the top site on O is related to the only energy minimum.

When differently coordinated oxygens are considered, the lowest coordinated atom is the preferred site for Pd binding, leading to the conclusion that steps in the support should be favored locations for clustering of the metal particle.

Relativistic Potential energy surfaces of small molecules and atomic clusters with heavy atoms

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We present full relativistic molecular calculations for the electronic and geometric structures of small molecules and atomic clusters consisting of very heavy elements using the all–electron Dirac-Fock–Slater method [1]. To get a high accuracy an improved calculation of the direct Coulomb potential has been taken into account by a special fit of the electronic charge density [2]. An example of the contour plot for the potential energy surface of Hg_3 is given in Figure 1. The knowledge of the gradients with respect to the nuclear coordinates is required to find the energy minmum by standard techniques [3]. Optimized geometries are not yet available in a full four–component formalism. We follow Satoko et. al. [4], who implemented analytical gradients for applications in nonrelativistic X_α–theories. Because of the incompleteness of our numerical four-component basis and because of the fitting procedure of the charge density additional terms result to the Hellman–Feynman gradient, which is the physical term describing the intermolecular forces.
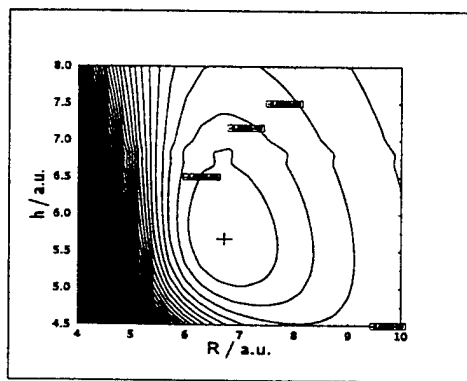We present first optimization results for a case with minimal basis set.

Figure 1: Contour plot of the potential energy surface of Hg_3.

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New Structure formation of Bare Boron Clusters

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New highly stable structures of bare boron clusters were constructed and determined using the most reliable theoretical methods derived from *ab initio* quantum-chemical and density functional theories. Our calculations were guided by basic conclusions obtained for elemental boron clusters [1,2] and by an "Aufbau Principle" proposed for a cluster formation. The new boron clusters have topologies different from the well known icosahedral α- or β-rhombohedral boron crystals. The final geometrical structures can be classified into the four groups: i) convex [3], ii) quasi-planar [4], iii) tubular [5], and iv) spherical clusters [3]. The cluster formation can easily be obtained from two basic units only, the pentagonal and hexagonal pyramids. The quasi-planar and tubular clusters, which are composed of dovetailed hexagonal pyramids only, can be considered as fragments of planar surfaces as in graphite or as sectors of extended cylindral pipes, respectively. In contrast, the convex and spherical clusters are composed of a combination of pentagonal and hexagonal pyramids. The convex clusters can be considered as segments of hollow spheres of different radii. The transition from quasi-planar or tubular into convex or spherical structures occurs only when pentagonal pyramidal units are included. In addition, nanotubular forms composed of dovetailed hexagonal pyramids were also found in α-boron quasicrystals [6].

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AB INITIO INVESTIGATIONS OF STRUCTURES AND ENERGIES OF SMALL SILVER CLUSTERS†

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Structures and energies of small Ag_n ($2 \leq n \leq 8$) clusters are studied within the framework of the density functional theory. A nonlocal hybrid functional - Becke's 3-parameter exchange and Lee, Yang and Parr's correlation - is used. Results for the bond lengths, binding energies and ionization energies are presented for different isomers. The calculations show that the transition from a planar to a three-dimensional geometry for the most stable isomer occurs at $n=6$. A detailed comparison with the results of earlier studies is presented.

Theoretical study of small Nickel clusters.

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The ground state geometries of small nickel clusters (Ni_{2-6}, Ni_8 and Ni_{13}) have been studied at the LCAO-LSDA level. As expected, many low lying states with different geometries or multiplicities has been found. From the results of our calculations we try to explain the bonding in these clusters by considering the participation of s and d type orbitals. The magnetic moment is found to change non-monotonically with size. Ni_5 is found to be highly magnetic while Ni_{13} shows a low magnetic moment. These results are in agreement with experimental results. Vertical photoabsorption spectra are also computed. Investigation on iron clusters are presently in progress. Special attention will be devoted to Fe_8 and higher size clusters.

Application and Extension of CEM Theory to Small Ni And Ionic Clusters

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Stable geometric structures and interactions energies of small clusters have been predicted using corrected effective medium (CEM) and MD/MC-CEM methods. In the non-self-consistent electron density functional based CEM theory, the interaction energy of a system containing N atoms, relative to the state in which all atoms are infinitely far apart, is given by

$$\Delta E(\{A_i\}) = \sum_{i=1}^{N} \Delta E_{EXLM}(A_i; n_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} V_c(i,j) + \Delta G(\{A_i\}) \qquad (1)$$

where the average electron density surrounding atom A_i is

$$n_i = \frac{1}{2} \sum_{j \neq i}^{N} \int \frac{n(A_i; \mathbf{r} - \mathbf{R}_i)}{Z_i} n(A_j; \mathbf{r} - \mathbf{R}_j) \, d\mathbf{r} \qquad (2)$$

Here, $n(A_i; \mathbf{r}-\mathbf{R}_i)$ is the atomic electron density at $\mathbf{r}$ for atom A_i with atomic number Z_i and nuclear position $\mathbf{R}_i$ and is obtained from Hartree-Fock calculations. $\Delta E_{EXLM}(A_i, n_i)$ is the embedding function for atom A_i determined by forcing Eq.(1) to duplicate the cohesive energy curve of the bulk and the homonuclear diatomic binding curve. $V_c(i,j)$ is the coulomb interaction between atoms, A_i and A_j, and is dependent only upon the already specified atomic electron density. ΔG is the difference in the kinetic-exchange-correlation energy between the real N-atom system and the N atom-in-jellium systems.

The simpler MD/MC-CEM method approximates the last term in Eq.(1) by the summation of values for each atom in a bulk system at the same value of n_i and incorporates this into an "effective" embedding energy. Application of this theory to small Ni clusters shows that the lowest energy structures do not resemble that of rare gas clusters or fragments of the bulk crystal lattice except where a stable icosahedral or bulk core is present. Experimental data exhibits very good agreement with our predicted structures for the number of equivalent low coordinated sturface atoms.

Results for small ionic clusters and species will be shown using a newly developed extension to the CEM theory. This extension includes the use of multiple densities per atom, where the density on atom A_i is

$$n(A_i; \mathbf{r} - \mathbf{R}_i) = \sum_{\alpha} C_{\alpha}(A_i) n_{\alpha}(A_i; \mathbf{r} - \mathbf{R}_i) \qquad (3)$$

This represents a linear combination of atomic densities in which $C_{\alpha}(Ai)$ is the coefficient of atom A_i with density n_{α}. The coefficients must be determined by variational minimization of the interaction energy.. This extension allows for the application of CEM theory to ionic species as well as to structures in which excited state densities contribute to the stability of the system. Development and application of this theory will be shown.

MAGNETIC MOMENTS OF IRON CLUSTERS: A SIMPLE THEORETICAL MODEL

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We present a simple model for the study of ferromagnetic transition metal clusters. Based on Fridel's model and on the geometrical characteristics, we obtain analytical expressions for the cluster average magnetic moment ($\bar{\mu}_N$) as a function of the number of atoms in bcc structures. The oscillatory behavior of $\bar{\mu}_N$ as a function of cluster size reported experimentally in Fe clusters is reproduced by considering *spherical* bcc clusters.

Theoretical Investigations on Zintl Clusters.

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The Zintl concept has been successfully used in the explanation of structures and bonding features of numerous condensed matter systems. In its widely accepted form due to Schafer et al., it states the structural invariance of an element under replacement of some of its atoms by another element with lower atomic number, provided the missing electrons are supplied through addition of alkali metal atoms which act as electron donors /1/. The work presented here focuses on the validity and applicability of the Zintl principle to antimony based atomic clusters which have been isolated by Knudsen Effusion Mass Spectrometry /2/.

In a series of computational studies, the properties of Zintl clusters derived from the extremely stable 20 valence electron unit Sb_4 are investigated. Special emphasis is given to systems of the form $ASnSb_3$ (A = alkali metal atom) and $HalTeSb_3$ (Hal = Halogen atom). As is demonstrated by Post-Hatree-Fock ab initio calculations, these species contain the Zintl anions $(SnSb_3)^-$ and $(TeSb_3)^+$, respectively, as cluster nuclei. Thus, the stabilization mechanism operative in these clusters involves alkali (halogen) components which serve as electron donors (electron acceptors). In all cases considered, electron transfer leads to the formation of clusters with Sb_4 analogous geometries and bonding features. Similar observations are made on molecules of the form $A_{2N}Sb_4$ (N = 1,2,3) with 22, 24 and 26 valence electrons. All of these systems turn out to be Sb_4^{2-} analogous, corresponding to strong electron transfer between the alkali and the antimony subsystems which results in a Jahn-Teller transition of the Sb_4 cluster nucleus from T_d to D_{4h} symmetry.

A third group of clusters analyzed here is of the form A_3Sb_3. For sufficiently high electronegativity difference between alkali and antimony components, these clusters can be shown to exhibit ozone analogous features.

In addition to the indicated alkali-antimony complexes, properties of the respective cluster nuclei will be discussed. Among these are frequencies for tunneling processes between different structural variants of Sb_4 and geometric phases accumulated by the electronic wave functions of Sb_3 molecules as these molecules undergo pseudorotation around a point of structural instability.

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Electronic and Geometrical Structure of Lanthanum Carbon Clusters

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Abstract

Endohedral complexes of metals (M) with Fullerenes (Bf)-M@Bf metallo-fullerenes - are subject of many theoretical and experimental investigations.

Much is known now about their structure and electronic structure, but there is a lack of knowledge on the formation of these systems. In the present contribution we have investigated theoretically rather small lanthanum carbon clusters ($LAC_n, n = 1 \ldots 6$). The understanding of the bonding and the structure formation in these carbon-metal clusters is a first step towards the understanding of the formation of the above mentioned metallofullerenes. Furthermore, such small clusters may play a role as precursors in the formation of the M@Bf.

We have performed Density Functional (DF) calculations within Local Spin Density (LSD) approximation and gradient corrections by using an LCAO treatment for the Kohn Sham orbitals. The geometries of several isomers of the La carbon clusters were optimized and the structure and electronic structure was analyzed. Generally, it turns out that the most stable structures are "π" complexes of the lanthanum with a "bent" carbon chain.

The trends in the structure and the bonding are discussed as a function of the number of carbon atoms. These results are compared with available experimental data. Further investigations towards larger clusters up to the endohedral complexes by itself are in progress.

MOLECULAR RESPONSE PROPERTIES AND ELECTRONIC EXCITATION SPECTRA FROM TIME-DEPENDANT DENSITY FUNCTIONAL RESPONSE THEORY

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Time-dependent density-functional response theory (TD-DFRT) provides a rigorous framework for the density-functional calculation of static and dynamic electric response properties, as well as electronic spectra, via the response of the charge density. TD-DFRT has been used in the context of the jellium sphere model to obtain information about the polarizabilities and photoabsorption spectra of alkali metal clusters since about the mid 1980s (see e.g. Ref. [1]). A molecular formulation of the same theory is desirable from the point of gaining information about the influence of the detailed molecular geometry on alkali metal cluster polarizabilities and spectra and for the treatment of more complex systems, such as transition metal clusters, for which the jellium sphere model is too rough an approximation. We have implemented TD-DFRT for molecular calculations [2, 3] and we will present results for small main group molecules from our continuing evaluation and amelioration of the method.

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On the role of interelectronic interaction in metal oxide clusters

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Response functions (hardness and softness tensors, dielectric and polarization response functions of a given state) are defined by using the $X\alpha$ method in the framework of metric geometry. The proposed model gives a comparatively simple approach to studying the interelectronic interaction (IEI) of a given orbital and shows the relationship between IEI and the electron density and electronegativity fluctuation.
The following transition metal oxide clusters were studied:

- $[Cr^{+3} O_6{}^{2-}]^{-9}$
- $[Fe^{+3} O_6{}^{2-}]^{-9}$
- $[Co^{+2} O_6{}^{2-}]^{-10}$
- $[Co^{+3} O_6{}^{2-}]^{-9}$
- $[Ni^{+2} O_6{}^{2-}]^{-10}$
- $[Cu_5{}^{+2} O_6{}^{2-}]^{-2}$

From the computed harness values the following conclusions can be drawn:

- the transition metal oxides (TMO) that have a degree of localization of the lowest 3d orbitals less than the maximum O2p hardness value exhibit metallic behaviour;
- the transition metal ions of lower valence state are more localized than those of higher valence states in the same lattice;
- The HSAB stability analysis shows that the 3d electron subsystems of model TMOs are unstable;
- the predominant 3d catalytic activation (e.g. for NO_2 decomposition reaction) is proportional to the difference of the hardness of 3d and valence electrons;
- the catalyst activation of anionic vacancies for adsorption of H_2O and NO is accomplished with a higher degree of localization of the valence electrons with the respect to the 3d electrons.

ENERGIES AND STRUCTURES OF GERMANIUM CLUSTERS*

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ABSTRACT

Gaussian-2 (G2) theory for third-row non-transition metal elements [L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, R. C. Binning, and L. Radom, J. Chem. Phys. **103**, 6104 (1995)] has been used to calculate the energies of germanium atom clusters, Ge_n (n=2-5). The equilibrium structures have been located and are in general agreement with previous theoretical studies. The G2 energies are used to calculate binding energies and enthalpies of formation of the clusters. The results are in reasonable agreement with the experimental enthalpies that have been measured for the clusters. The trends in fragmentation energies for the germanium clusters are compared to those calculated previously at the G2 level of theory for silicon and carbon clusters [K. Raghavachari and L. A. Curtiss in Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy, S. R. Langhoff, editor (Kluwer Academic Publishers, Dordrecht, 1995) p. 173.].

Defects and Energetics of Si Quantum Dots: A Real Space Approach

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We use the higher-order finite difference pseudopotential method for *ab initio* study of optical properties of Si quantum dots. The calculations are performed in real space using spherical bulk-terminated clusters containing up to 15 shells of Si that are passivated by hydrogens at the boundaries. The main advantages of a real space approach in this study are easy calculations of the excitation energies and dielectric functions. We calculate the size dependence of the HOMO-LUMO gap and compare with available calculations. We also investigate quantum confinement effects in other optical properties of Si quantum dots such as excitation energies, oscillator strengths, and dielectric functions.

Silver cluster/ammonia complexes

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Silver cluster/ammonia complexes are becoming one of the best experimentally characterized metal cluster molecular association complex systems. We report on their investigation on several fronts including: the gas-phase kinetics of their formation; their infrared photodepletion spectroscopy; and their ultraviolet photodissociation dynamics.

The kinetic studies lead to quantitative thermochemical information on the interaction including binding enthalpies and entropies. These properties are strongly size dependent and lead to conclusions regarding the degree of mobility of the ammonia ligand on different cluster surfaces. The infrared photodepletion studies probe the cluster size and degree of coordination dependence of the NH_3 umbrella stretch frequency. These dependencies demonstrate the sensitivity of this mode to details of the binding site. There is, however, no obvious correlation with the electronic properties of silver clusters or with the binding energy of the complex. Evidence for cooperative binding and equivalent and non-equivalent binding sites are found in particular cases. The infrared depletion dynamics are of interest because of the parallel with infrared and thermal desorption from surfaces.

The ultraviolet photodissociation dynamics have been studied in some detail for the silver dimer ammonia complex and are being extended to larger clusters. They provide a basis for comparing photodesorption from clusters to that from surfaces.

Nano-scale Modification of Silicon Surfaces via Coulomb Explosion

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Coulomb explosions on silicon surfaces are studied using large-scale molecular dynamics simulations. Processes under investigation begin by embedding a region consisting of 265 - 365 singly charged Si^+ ions on a Si [111] surface. The repulsive electrostatic energy, initially stored in the charged region, leads to a local state with ultrahigh pressure and stress. During the relaxation process, part of the potential energy propagates into the surrounding region while the remainder is converted to kinetic energy, resulting in a Coulomb explosion. Within less than 1.0 ps, a nanometer-sized hole on the surface is formed. A full analysis of the density, temperature, pressure and energy distribution as functions of time reveals the time evolution of physical properties of the systems related to the violent explosive event. A shock wave that propagates in the substrate is formed during the first stage of the explosion, $0 < t < 100$ fs. The speed of shock wave is twice the average speed of sound. After the initial shock, the extreme non-equilibrium conditions lead to ultra-rapid evaporation of Si atoms from the surface. Our simulations demonstrate the details of a processes that can lead to permanent structure on a semiconductor surface at the nanoscale level. The work reported here provides physical insights for experimental investigations of the effects of slow, highly charged ions ($Q > 40$, e.g.) on semiconductor materials.

C_{60} spectrum within the free-electron model

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The new model is applied to the calculation of the single electron energy spectrum of the fullerene. The theory states the correspondence between the tight-binding framework and the model of the free electrons on the molecular orbitals. The simplicity of the spectrum analysis coincides with the explicit group-theoretical approach in the model. The generalization of the model for the external field applied is discussed.

Paradoxical Magnetic Cooling

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Cooling to ultralow temperatures is presently achieved using the isentropic demagnetisation process suggested in 1926 by Debye and Giauque [1,2]. Here we introduce a system which does not cool, but rather heats up during isentropic demagnetization. This classical system, consisting of several magnetite particles in a colloidal suspension, shows the uncommon behavior of disordering structurally while ordering magnetically in an increasing magnetic field. We propose to use the structural disordering in high fields to cool a system by isentropic magnetisation instead of demagnetisation. Whereas analogous systems with a large number of particles, the ferrofluids, have been discussed previously as candidates for use in magnetocaloric heat engines [3], the occurrence of the paradoxical magnetic cooling phenomenon is unique to systems with only few particles.

Plasmon in carbon bi(tubule) by tight binding calculation

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Experimently tubule have been largely investigated with the Electron Energy Loss Spectroscopy (EELS) which gives some insights on the σ and π plasmons. In the present contribution, they bill be analized in the tight binding approach. The Hamiltonian modelising the tubule will take account of the σ and π electrons (i.e. s, Px, Py, Pz orbital components).

The dielectric constant of the tubule B(0,1)n (n is the number of hexagons on the circumference) will be derived in the Random Phase Approximation versus n leading to the determination of the plasmons. The EELS spectra proportional to $\text{Im}\left(\dfrac{1}{\varepsilon}\right)$ will be examined. Finally the case of the bitubule will be examined.

Plasmon in carbon cone structure

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Single (multi) shell carbon cone have been reported by Sattler during a new chemical synthesis of tubule by vapor phase deposition. They have been imaged with the atomic resolution scanning tunneling microscopy and atomic force microscopy. The measured β cone angle takes some discrete values (19.2, 30.9, 60, 88.6 and 133.6).

If we compare with the tubule case, the tubule characterization was up to now mostly carried out with high resolution microscopy. So electron energy loss spectroscopy has brought some insight on the π and σ plasmon in tubule.

The present contribution deals with the characterization of the plasmon in carbon nanocone with the cone symmetry Hamiltonian. The plasmon has been investigated by studying the dielectric function $\varepsilon(q,\omega)$ derived within the Random Phase Approximation. The dependence of the angle β on the plasmon will be examined.

Finally the electron loss spectra has been calculated.

THE CHEMISORPTION OF OXYGEN AND HYDROGEN ON THE GRAPHITE SURFACE STUDIED BY THE CLUSTER MODEL APPROACH.

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The atomic models of up to 48 carbon atoms [1] are used to simulate the chemisorption of oxygen and hydrogen on the graphite surface. The calculation are based on both INDO method and on the semiempirical potentials. The minimum of the potential energy between the H adatom and the surface was found at INDO level of approximation, above the carbon atoms at a distance of about 1.25A. The lowest activation energy for migration of H has been obtained for a route above C-C bonds , being about 4kcal/mol. Its value is higher for the migration of the adatom across the carbon ring (about 10 kcal/mol). The equilibrium positions and barrier migration between them have been calculated in the case of oxygen/graphite system. The results of this study are compared with those obtained by the embedding approach in chemisorption [2]. The investigation on the vibration modes of chemisorbed H and O atoms on the graphite basal plane has been carried on. The vibration modes of adsorbates have been calculated using the adatom - surface potential resulted from quantum calculations, and a semiempirical Tersoff's potential [3] for the interaction between carbon atoms. The adatoms contributions to the density of states of the graphite surface were investigated in relation with the localisation of the unielectronic wave function on the adsorbate. An extended cluster model has been used to consider the effect of the second graphite plane on the H and O chemisorption. We investigated the behaviour of the isolated hydrogen molecule orientation versus the distance to the surface. The molecular hydrogen has the same chemisorbed position as the atomic species. H2 reaches the minimum of the potential energy for a vertical orientation at 2.25A above carbon atoms. An analysis on the anisotropic potential shows that the isolated H2 molecule has the lowest activation energy for a precessional rotation around the normal direction to the surface. The hindered rotation i.e. the libration and precession of an isolated adsorbed molecule is studied as an effect of the anisotropic potential obtained for H2/graphite system. The interactions with the frozen first order adsorbed H2 neighbours are considered in an extended model. The vibrational analysis of the proposed cluster model has been compared with the in plane phonons of the hydrogen /deuterium monolayer experimental data. An analysis on the parameters values used at the approximation level of AM1 and PM3 used on physisorbtion on the graphite surfaces is also included.

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HYDROGEN SATURATED CLUSTER MODEL STUDY OF THE SUBSTITUTIONAL IMPURITIES RELATED DEFECTS IN SILICON

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The $X\text{-}Si_n\text{-}H_m$ (n = 4, 16, 40) cluster models [1] have been used on studding the properties of substitutional impurities related defect in silicon. Hydrogen atoms were used to remove the dangling bonds at the border of the silicon cluster and for simulating the environement in the crystal. This study deals with both the relaxation of the host lattice around a substitutional impurity atom and with its electronic structure. The local vibration mode couples the Si neighbours of the impurity, especially those involved in relaxation. Two aproximations of the lattice relaxation process have been considered by involving only the first Si neighbours or both the first and the second ones. The influence of the host crystal is modelled by considering a fixed Si and H atomic cage. The bond length in the relaxed core of pure silicon cluster model has been calculated versus the radius of the cage. The value of atomic cluster radius, that corresponds to the same relaxed Si-Si bond length as in bulk Si (2.35A) is considered. The Td symmetry was imposed. The N,C,Ge,As and P related defects in Si have been studied by using a model having the impurity atom in the centre of the cluster. The Si neighbours displacement around the substitutional impurities have been calculated by using the same cage radius that assures the bulk Si-Si bond length in pure Si relaxed clusters. An extensive analysis on different approximation levels of the LCAO semiempirical methods have been carried out. The best results are obtained using PM3 and AM1 methods. The relaxation displacements of the nearest Si host neighbours have been calculated for the above mentioned substitutional impurities. The results based on the PM3 method are in good agreement with those obtained by the Green's function approach [2]. The states localised at the border of the cluster (Si-H bonds) are interesting for the investigation of $Si\text{-}H_x$ hydrides vibration modes on the surface of silicon crystal. The vibration modes of Si-H and Si-H2 have been calculated in the frame of pure hidrogenated silicon cluster model. The results based on LCAO quantum mechanical theory have been compared with those obtained by using semi-empirical potentials for Si [3]. The IR data of the hydrogenated porous silicon and the active vibration frequencies of the substitutional impurities in Si have been related with the theoretical results based on the atomic cluster model approach.

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Probing the Electronic Structure Evolution of Transition Metal Clusters from Atoms to Bulk*

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The electronic structure of transition metal clusters is important in understanding the chemical and physical properties of these clusters and has presented considerable challenges both experimentally and theoretically. Photoelectron spectroscopy of size-selected cluster anions has emerged as a powerful experimental technique to probe the electronic structure of metal clusters over a wide size range. Recent advances in our laboratory has allowed us to obtain considerably detailed electronic structure information for all the first row transition metal clusters. For the first time, we are now able to follow the evolution of the electronic structure of the transition metal clusters from the atoms to the bulk in great detail. Successful theoretical interpretation of the experimental photoelectron spectra will provide a complete understanding of not only their structure and bonding but also their other physical and chemical properties.

In this contribution, we will present our recent experimental results for the first row transition metal clusters from Ti_n to Ni_n containing up to 70 atoms. For the Ti clusters, we observe that the electronic structure becomes bulk-like above n=8 due to the significant delocalization of the 3d orbitals in Ti.[1] For the V clusters, distinct transitions from molecular-like to bulk-like electronic structure is observed. For n=2-12, the V clusters can be viewed as molecules each with its different electronic structure. At n=17, the bulk-like features appear abruptly, and for n>65 the cluster photoelectron spectra become indistinguishable from that of the bulk. The clusters in the size range from n=13-16 provide the transition size range from the molecular-like to the bulk-like behavior and the spectral features can be followed from one cluster to the next.

For Cr clusters, we observe surprisingly even-odd alternations in the photoelectron spectra and the electron affinities of the clusters for n=1-11. The even-odd alternations in the electronic structures of the small Cr clusters are interpreted successfully by a dimer growth route of the cluster structures discovered through an extensive and systematic density functional theory investigation, that also predicts a structural transition from the dimer growth to bulk-like body-centered cubic structures from n=11 to 12 and the nature of the antiferromagnetic coupling in the small Cr clusters.[2]

For the ferromagnetic (superparamagnetic) clusters of Fe, Co, and Ni, extensive electronic features are observed for the Fe clusters even for n >20 while such features become more difficult to resolve for the Co and Ni clusters which show broad photoemission features for n>13 with no resolvable fine structures. The Co and Ni clusters show similar electronic features, consistent with the fact that they also exhibit similar magnetic properties. For example, both Co_{13} and Ni_{13} show abruptly narrow photoemission bands, in agreement with their having high I_h symmetry. The electron affinities of small Ni clusters from n=1-4 show even-odd alternations similar to that of Cu clusters, suggesting that the 3d electrons in small Ni clusters are localized and the bonding are predominantly of 4s character. There is also evidence that Ni_3^- has two isomers, a linear one and a triangular one.

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Transitions of clusters with short-range interactions of atoms to bulk particles.

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The growth of large solid clusters with short-range interactions between atoms is the subject of analysis. This type of atom interactions is an object of interest by two reasons. First, because it models interactions of inert gas atoms at some conditions better than the Lennard-Jones interaction potential. Second, one can consider only interactions between atoms - nearest neighbors and this simplifies the analysis significantly.
A large cluster differs from a bulk particle by discontinuous dependence of its parameters on a number of atoms. When fluctuations of cluster parameters exceed the nonregularity due to the cluster structure, the cluster is considered as a bulk particle. Here as a cluster parameter we take the total binding energy of cluster atoms. The transition cluster -> bulk particle is expected to take place at number of cluster atoms n > 1000 for the face-centered cubic cluster structures. The basis of such cluster at zero temperature is tetradecahedron (a regular truncated octahedron which surface consists of 6 squares and 8 regular pentagons). This surface is covered partially by atoms. The optimal cluster configurations and binding energies are found for each number of atoms in the region n = 1289 - 2406. One can find the asymptotic expression for the binding energy and its fluctuation with the size of the cluster from this data. As a second step the fluctuations of cluster energy for the small temperatures are estimated using the harmonic oscillations of cluster atoms and the cluster configuration transitions from optimal to close to the optimal. The comparison of the above fluctuations helps us determine at what temperature and size the transition cluster -> bulk particle takes place.

A Cluster Model for the Investigation of Localized Properties of Impurity Center in Solid Systems

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The Unrestricted Hartree-Fock (UHF) Cluster Procedure was used to simulate a selected region of interest around an impurity center in the bulk of La_2CuO_4 crystalline environment. In the present work, the impurity center is a [111]Sn replacing a copper. The cluster procedure was applied to obtain the electronic structure of the system and to study the magnetic hyperfine field that serves as a test for the applicability of the cluster method. A Cu_4SnO_6 cluster was chosen to represent the region of interest. It consists of a central Sn surrounded by four planar oxygens that form a plane with Sn, two apical oxygens (one directly on top and one below Sn), and four copper ions at sites equivalent to the central Sn site. In the UHF cluster procedure, the number of atoms or ions that can be included in the cluster is normally limited to make the calculation of the electronic structure feasible. Boundary conditions are applied so that the effects of the rest of the solid environment around the chosen cluster are properly simulated. In our work, the Cu_4SnO_6 cluster was embedded in an assembly of formal point charges at the lattice sites. The charges on the outermost shells were adjusted so that the correct Madelung potentials are reproduced and at the same time maintaining the charge neutrality of the entire system. The converged wave functions were used to calculate the magnetic hyperfine field at [111]Sn which comes out to be -15.48 kOe, 0.19 kOe and 1.2 kOe for the contact, dipolar and point dipole parts respectively giving a total hyperfine field of -14.09 kOe. Our calculated result for the hyperfine field compares reasonably well with the measured experimental magnitude of about 8.7 kOe [1]. The effective charges on the ions in the cluster after self consistency is achieved are calculated to be 2.93, -1.86 and -1.89 for Sn, planar oxygen and apical oxygen respectively. The convergence of the wave function with respect to the cluster size was tested using the pure system in which two different sizes of clusters were used, a CuO_6 cluster and a Cu_5O_6 cluster. We found that the hyperfine field at [63]Cu site does not change appreciably in going from the small cluster to the bigger one, indicating a good convergence with respect to cluster size. We have found from our investigations that the cluster procedure can be used to study localized properties both in pure systems as well as impurity centers in solid environment. The nature of the bondings including the extent of covalency effects, and also lattice relaxation effects due to the presence of impurity centers can be studied using this cluster procedure.

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$C_{60}O$ and $C_{60}O_2$: Thermodynamics vs Kinetics of Formation

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$C_{60}O$ has consistently been computed in a disagreement with observations - the ground state of the system is computed as a 5/6 species while in the experiment only a 6/6 structure can be seen. The facts cannot be explained through temperature (i.e., entropy) factors. The problem becomes even more serious with $C_{60}O_2$. Its twenty isomers are studied by the AM1 quantum-chemical method. Their full geometry optimization is performed, and also vibrational harmonic analysis and evaluation of relative concentrations at selected temperatures is reported. The computations again cannot identify the computed ground state with the observed species (6/6 6/6) as among the bridged structures a 5/6 5/6 isomer is the lowest in energy. At this stage we have approached the disturbing problem as a possible kinetic control of the relative stabilities (i.e., not only temperature but also time factor should be reflected). Activated complexes are rigorously described in theory and can be located with some special effort. Using the computed activation parameters we can put theory and observation in agreement for the first time and view the oxides formation as a special case where activation energy order is reversed compared to the standard thermodynamic terms. There are two principal isomers for the $C_{60}O$ itself, either created by bridging a 5/6 bond between a pentagon and a hexagon or a 6/6 bond between two hexagons. The 5/6 mono-adduct is lower in energy and its critical 5/6 bond is broken, however, in experiment only the 6/6 mono-adduct was observed. This serious disagreement between theory and experiment has never been explained. We could allocate activated complexes for the 5/6 and 6/6 mono-adduct formations. In fact, they are not of epoxo but rather of keto forms. The activation energy for the 6/6 path is lover by 12.4 kcal/mol than that for the 5/6 path. It means that, for example, at room temperature the 6/6 isomer must be almost exclusively formed during the initial stages of the reaction. Only relatively very long reaction times can allow for a thermodynamic equilibrium. Let us note that the activation entropy changes nothing on the picture at room temperature. Hence, we suggest that the formation of the mono-adduct is kinetically controlled in the available experiments. This finding also plays a key role in understanding the dimer formation. In particular, it eliminates the 5/6 5/6 dimers on the kinetic ground in spite of the fact they are quite low in thermodynamic stability scale. The 5/6 isomer has C_s symmetry and this allows for 48 possibilities for bridging with the second oxygen atom. In the more symmetric 6/6 isomer (C_{2v} symmetry) we have only 28 possibilities for the second bridging. If we start with a common ring, the three lowest-energy structures are of the 5/6 5/6 type and the highest structure in energy exhibits the 6/6 6/6 pattern. Other structures (diketo, vertical, peroxo) are to be considered, too. Nevertheless, a deeper kinetic analysis indeed points out the 6/6 6/6 species with the oxygen atoms on one common hexagon as the most important structure in the kinetically-controlled experiments. A thermodynamically equilibrated experiment would be a final test.

Mesh Hartree-Fock Calculations of Non-Spherical Metal Clusters in the Jellium Model

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Most theoretical works which consider metal clusters in the framework of the jellium model use the assumption of their spherical symmetry. But this assumption could not be taken for granted a priori. In the simplest case of a system with two non-localized electrons the jellium-model cluster could be theoretically considered both as some helium atom-like system and as a system similar to the hydrogen molecule. The choice between these models could be made only on the basis of calculations of the energies of these systems. We present here the results of calculations of metal clusters in the framework of the jellium model. The positive charge of the core is presupposed to be distributed in an ellipsoidal box with disperse edges. The spatial distribution of the charge was taken in the

form $P(\rho,z) = A \cdot \left\{ 1 + \exp\left[\left(\sqrt{\rho^2 + (zb)^2} - a \right) / \Delta r \right] \right\}^{-1}$, where (ρ,z) are cylindrical

coordinates, A is the normalization parameter, $a = r_\rho$ - core radius for ρ direction, b - non-sphericity parameter $b = r_\rho / r_z$, and Δr is the length of the disperse charge region. We express all values in atomic units. The subject of our calculations was the total energy, which is the sun of the electrostatic core energy and the Hartree-Fock energy of non-localized electrons $E_{tot} = E_{core} + E_{el}$. This system have no spherical symmetry and cannot be constructed of separate atoms. The calculations of E_{el} for the system were carried out by means of the mesh Hartree-Fock method based on [1,2] and modified for better calculations of systems with distributed positive charge. The results of calculations for the simplest two electron clusters are presented in the Figure as a map of E_{tot} values in (a,b) coordinates. The calculations show that the minimum of E_{tot} is $E_{tot} = -0.106$ at $a = 4.6$, $b = 0.6$, i.e. $r_z = 7.7$, $r_\rho = 4.6$ (for $\Delta r = 0.5$). Thus, the two-electron jellium-model cluster appears to be a non-spherical system rather similar to the hydrogen molecule. The analogous Hartree-Fock calculations for the ellipsoidal clusters with more than two electrons show that their forms are dependent on the number of electrons and their quantum states.
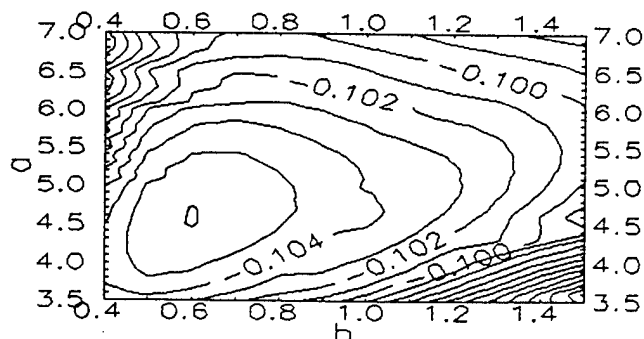
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Chemical Reactions of Semiconductor Clusters

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Abstract

Smalley and co-workers discovered that chemisorption reactivities of silicon clusters vary over three orders of magnitude as a function of cluster size. In particular, they found that Si_{33}, Si_{39}, and Si_{45} clusters are least reactive towards various reagents compared to their immediate neighbors in size. We explain these observations based on our stuffed fullerene model. This structural model consists of bulk-like core of five atoms surrounded by fullerene-like surface. Reconstruction of the ideal fullerene geometry gives rise to four-fold coordinated crown atoms and π-bonded dimer pairs. This model yields unique structures for Si_{33}, Si_{39}, and Si_{45} clusters without any dangling bonds and thus explains their lowest reactivity towards chemisorption of closed shell reagents. This model is also consistent with the experimental finding of Jarrold and Constant that silicon clusters undergo a transition from prolate to spherical shapes at Si_{27}. We justify our model based on an in depth analysis of the differences between carbon and silicon chemistry and bonding characteristics. Using our model, we further explain why dissociative chemisorption occurs on bulk surfaces while molecular chemisorption occurs on cluster surfaces. We also explain reagent specific chemisorption reactivities observed experimentally based on the electronic structures of the reagents. Finally, experiments on $Si_x X_y$ (X = B, Al, Ga, P, As, AlP, GaAs) are suggested as a means of verifying the proposed model. We predict that $Si_x(AlP)_y$ and $Si_x(GaAs)_y$ ($x = 25, 31, 37; y = 4$) clusters will be highly inert and it may be possible to prepare macroscopic samples of these alloy clusters through high temperature reactions.

ON THE MECHANISMS OF CLUSTERS SPUTTERING
FROM THE FROZEN WATER SOLUTIONS

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The pattern of clusters, sputtered from the frozen water
solutions of organic and inorganic compounds under the
accelerated particles impact in mass spectrometric experi-
ment, may provide information precious for ecological and
cryobiological studies. However the interpretation of the
low temperature (LT) fast atom bombardment (FAB) mass
spectra is rather difficult due to their complexity and
substantial changes with temperature variations. In the
present communication a model of clusters sputtering under
the LT FAB conditions is presented, which allows to make
correlations between the physico-chemical parameters of the
frozen solid and the corresponding clusters pattern. It is
known, that water solutions of different compounds undergo
phase separation upon cooling in accord with the inherent
phase diagrams. Analysis of the available data on the mor-
phology of the frozen water solutions showed, that the mean
dimensions of the structural elements of the heterogeneous
solid (crystallites, intergrain channels) are one-two orders
of magnitude larger than those of the zone disturbed by the
impact of a single bombarding particle. Due to this fact
each impact of a particle causes the sputtering of clusters
from the surface domains, containing individual components
of the separated mixture. In such a situation the cluster
are composed only of the molecules (ions) of one type, and
the formation of heterogeneous clusters immediately points
either to formation of some kind of new compound under
freezing or to homogeneous amorphyzation. The examples of
the application of the proposed model to attribution of
clusters sputtered from the frozen water solutions of the
salts of alkali metals, acids, glycerol, ethanol, nitrogen
bases are discussed.

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Notes

TIME	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
8:20 a.m.	OPENING REMARKS				
8:30	D. Wales	E. R. Hilf	U. Landman	A. Rosén	S. Khanna
8:35	Z. Bačić	J. D. Doll	C. Guet	J. A. Alonso	P. Jena
9:15	L. Wöste	M. Jarrold	K. M. Ho	H. Häkkinen	J. R. Chelikowsky
9:40		Coffee Break			Coffee Break
9:55	Coffee Break		I. Garzón	Coffee Break	
10:10					
10:20			Coffee Break		
10:30	R. B. Gerber	D. H, E. Gross		P. Hackett	J. Jortner
10:50			G. M. Pastor		
11:00					Lunch
11:10	U. Landman	S. Srinivas		M. Moseler	
11:30			S. Khanna		
11:35	G. Seifert	H.-P. Cheng		R. J. Tarento	
11:55			T. Frauenheim		
12:00	Lunch	Lunch		Lunch	DEPARTURE
12:20			Lunch		
2:00 p.m.		K. H. Bennemann	BOAT TRIP	M. Manninen	
2:05		C. Yannouleas		V. Bonačić-Koutecký	
2:45		K. A. Jackson		R. Kawai	
3:10		K. Raghavachari		Coffee Break	
3:35		Coffee / POSTERS			
3:40				M. E. Garcia	
4:20				I. G. Kaplan	
4:30	Coffee				
4:50	C. Guet				
4:55	W. L Hase				
5:35	M. J. López				
6:30	Dinner	Dinner	Dinner		
7:30				Banquet	
7:45	POSTERS	ROUNDTABLE DISCUSSION	ROUNDTABLE DISCUSSION		
8:00		D. R. Salahub E. Carter K. Raghavachari A. Rosén N. Russo	R. S. Berry I. Ohmine J. N. Onuchic D. Wales		